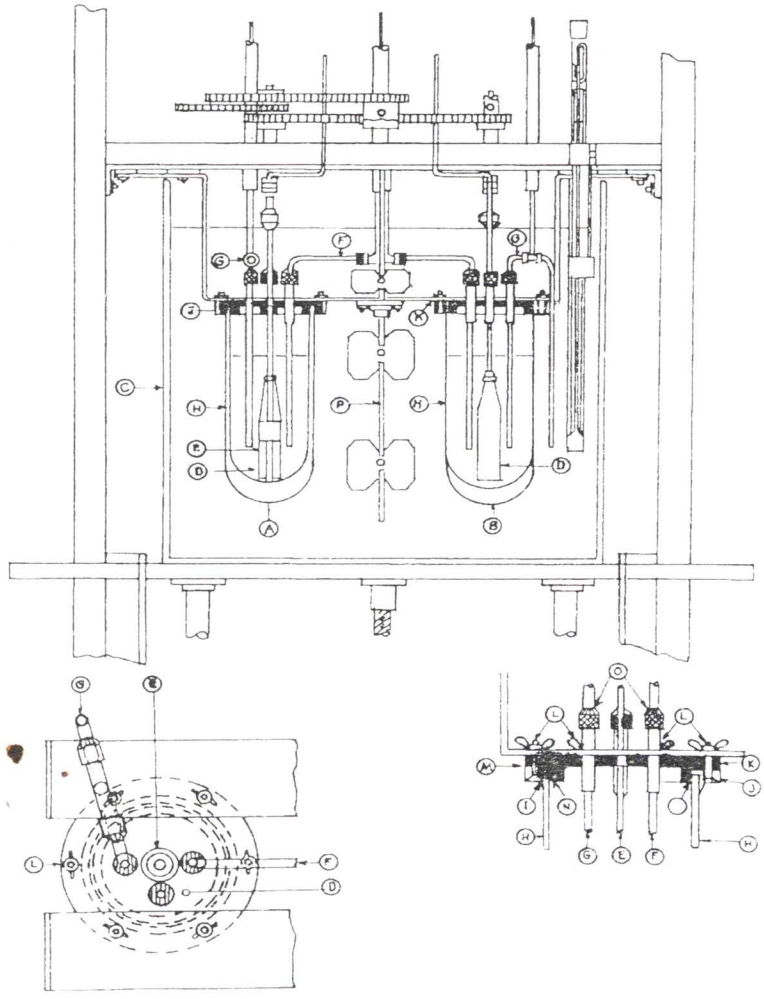
IOAN GĂINAR DANIELA BALA

CHEMICAL THERMODYNAMICS
THEORY AND APPLICATIONS



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CHEMICAL THERMODYNAMICS THEORY AND APPLICATIONS

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INTRODUCTION

In writing this book, it has been our aspiration to produce a volume, which will be the students to master the most important problems in chemical thermodynamics. The book is designed primarily for students that study chemistry in English language. This book is not intended to be a treaty in chemical thermodynamics. It is assumed that the reader already knows the notions that work, heat, internal energy etc and the basic laws of thermodynamics.

Thermodynamics is a subject that can be studied more that once to good advantage, for many of the abstract concept become fully appreciated only after repeated consideration. The subject has an excellent balance of logical deductions and widespread application.

The book is divided into three parts. At the beginning we present the notion of temperature and the methods that allow measuring it. The first part, a theoretical one, is a tight connection with the second and third parts that include experimental works and problems, respectively.

In the theoretical treatise of this subject we have started from the fundamental idea in thermodynamics: this states that the chemical potential of particular component present in more then in one phase in an equilibrium system is the same in each phase. This idea is one of the most powerful statements known to science.

The theoretical part includes four chapters:

I. The deviations from the ideal behavior (partial molar quantities, the compressibility factor);

II. Fundamental notions of calorimetry;

III. Chemical equilibrium (free energy of reaction, equilibrium constants and equilibrium displacement, electrochemical equilibrium);

IV. Phase equilibria (fundamental relations, mono-, bi- and three- components equilibria).

The second part of this book includes seventeen experimental works (chapter V), judicious chosen, so that they will totally cover the fundamental ideas introduced in the theoretical statement.

The textual material is intended to be sufficiently complete to provide a basic knowledge of more important chapters of chemical thermodynamics, but a full appreciation of the subject can be gained only by working numerous problems. A substantial number of numerical applications have been incorporated in the chapter VI of this book.

The authors

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TEMPERATURE AND ITS MEASUREMENT METHODS

Temperature is one of the most important variables in thermodynamics and physical chemistry.

TEMPERATURE SCALES

The *thermodynamic temperature scale*, based on the second law of thermodynamics, embraces the Kelvin (absolute) scale and the Celsius scale, the latter being defined by the equation:

$t_{Celsius} = T_{Kelvin} - 273.15$

The size of the Kelvin degree is defined by the statement that the triple point of pure water is exactly 273.16 K. The practical usefulness of the thermodynamic scale suffers from the lack of convenient instruments for measuring absolute temperatures routinely to high precision. Absolute temperatures can be measured over a wide range with the helium gas thermometer (appropriate corrections being made for gas imperfections), but the apparatus is much too complex and the procedure much too cumbersome to be practical for routine use.

Since the triple point of water is defined to be exactly 273.16^0 K on the thermodynamic temperature scale, this is an especially important fixed point. It is also a point, which can be reproduced with exceptionally high accuracy. The temperature of the triple point is reproducible within the accuracy of current techniques (about $\pm 0.00008^0$ C).

THERMOMETERS

Mercury thermometers

So far the most common type of laboratory thermometer is the mercury thermometer, based on the differential volume thermal expansion of liquid mercury (about 1.8×10^{-4} deg^{-1}) and glass (about 0.2×10^{-4} deg^{-1}). In the manufacture of such thermometers, the stem, a capillary of uniform bore, is usually marked at two points (say 0 and 100^0 C) and then graduated uniformly in between. It is assumed that the volume of a fixed mass of mercury in glass is a linear function of the temperature. The

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error resulting from this assumption is ordinarily smaller than due to variations in the bore of the capillary.

Important sources of error in mercury thermometers are parallax and sticking of the mercury meniscus. The first can be largely avoided by careful positioning of the eye when reading or use of a properly designed attached magnifier. It can be eliminated entirely by use of a cathetometer. Sticking of the mercury meniscus is due to the fact that the contact angle of mercury to glass varies depending on whether the mercury surface is advancing or receding, and thus the capillarity pressure due to surface tension is variable. This combines with the small but finite compressibility of the mercury and the elasticity of the glass to yield a small variability in meniscus position, especially for very sensitive thermometers. Gentle tapping of the steam before taking readings usually leads to reproducible results. Readings of sensitive mercury thermometers are also slightly pressure dependent; pressure coefficients may be as high as 0.1 deg atm^{-1}.

When precision of better than about 1 percent of full scale is required, it is necessary to use a calibration chart, which gives corrections to be added to or subtracted from the readings.

Special thermometers are made for calorimetric work, where it is to desired to measure very accurately (to 0.01 or even 0.001^0) a temperature *difference* of the order of a few degrees. For these thermometers the fineness of scale graduation has little to do with the accuracy with which the thermometer measures a single temperature.

Beckmann thermometer

The Beckmann thermometer is a *differential* thermometer with a range of 5 or 6^0 and graduations of 0.01 or 0.02^0. It differs from an ordinary thermometer principally in having a provision for changing the position of this 5 or 6^0 interval on the temperature scale by adjusting the amount of mercury in the bulb and thread. For this purpose a special reservoir is provided at the top of the thermometer (see figure 1).

To rise the setting, the bulb is warmed so as to discharge droplets of excess mercury into this reservoir. To lower the setting, the bulb is warmed to bring the mercury thread into the bottom of the reservoir, where it is then united with a column of excess mercury which is brought into position by inverting the thermometer. The bulb is cooled to draw mercury into the thread. At a few degrees about the desired range the excess mercury is broken away from the thread by a sharp tap with the fingers.

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The thermometer is then brought to an upright position in such a way as to bring the excess mercury to its normal position in the reservoir.

Since the cubical expansion coefficient of mercury is not exactly constant, the magnitude of the true temperature difference represented by a scale division of the Beckmann thermometer varies with the temperature at which the thermometer is set to operate; accordingly, correction are required in precision work. For a Beckmann thermometer made of Jena 16 glass (which may be taken as representative of German-made Beckmann thermometers), having a calibration which is valid when the midpoint of the scale is 20^0 C, a temperature difference measured at temperature t can be corrected by multiplication with the factor $1 + 3x10^{-4} (t - 20) - 10^{-6} (t - 20)^2$.

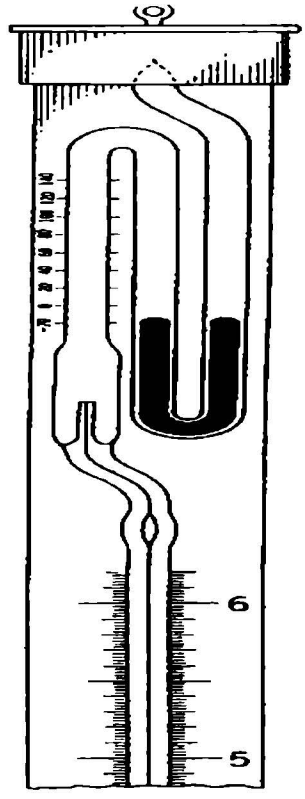

Figure 1. Upper end of Beckmann thermometer

The Beckmann thermometer is very fragile and often subject to difficulties in use. Its use is best reserved for special purposes not served by available fixed-scale thermometers. Fixed-scale thermometers are ordinarily preferable for calorimetric and cryoscopic work in the usual temperature range.

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Platinum resistance thermometers

The platinum resistance thermometer is capable of extremely high precision, owing to the high purity attainable for platinum and the high reproducibility of its temperature coefficient of resistivity. The resistance element is a coil of pure platinum wire, carefully annealed both and after winding and enclosed in a tube (usually of glass) containing dry air or helium as a heat-transfer gas. Two leads are ordinarily attached to each end of the coil, in order to permit the resistance of the coil to be measured independently of the resistance of the leads. Platinum resistance thermometers in glass housings containing dry air may be used from – 183 to 500^0 C or with a special glass housing to 630.5^0 C. the coil resistance is determined by means of a Wheatstone bridge of appropriate design.

Thermistors

Thermistors are semiconductor devices consisting of sintered mixtures of metallic oxides (such as NiO, Mn_2O_3, Co_2O_3). These ceramic-like resistors have large negative temperature coefficients of resistivity; the variation of the resistance R can be roughly approximate by:

$$R = R_\infty \cdot e^{\Delta E/kT}$$

where ΔE is the electron energy gap. For a typical thermistor, $\Delta E/k \approx 3500$ deg, which means a change in resistance of 4 percent deg^{-1} at room temperature. Thus, the magnitude of R^{-1} (dR/dT) is about 10 times that of metallic resistors and high precision as a resistance thermometer can be attained with a less sensitive bridge than is required for a platinum thermometer. In addition, the resistivity is so high that thermistor elements can be very small without introducing serious complications due to lead and contact resistances. An important advantage of the small size of thermistors is their low heat capacity and rapid temperature response. Two disadvantages of thermistors in comparison with a platinum thermometer are their lower reproducibility and their poorer long-term stability.

Thermocouples

Thermocouples provide one of the most convenient means of measuring temperatures over a wide range from very low (- 250^0 C) to very high (1700^0 C) values. All that is required is a pair of wires made from two suitable metals or alloys, a good potentiometer, and a constant-temperature bath (usually an ice-water bath) for the reference junction.

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When two dissimilar metals are placed in contact, a transfer of electrons from one to the other takes place and a double charge layer forms at the junction surface. As in the case of a junction between a metal electrode and an electrolyte solution, the resulting electric potential must be measured in the presence of a reference junction, which in the present instance is a junction of the same two metals at a known temperature. The thermoelectric potential is measured between the ends of two wires of the same metal-one wire leading to the junction at the reference temperature and the other to the junction at the unknown temperature; the two junctions are connected directly by a wire of the second metal completing the circuit. This potential is a measure of the unknown temperature, and in cases where the temperature difference is not large, it is roughly proportional to the difference between the unknown and reference temperatures.

The most useful thermocouple for general work is *cooper – constantan*, the latter being an alloy of 60 percent copper and 40 percent nickel. An important advantage of the use of this couple is that one of the metals is copper, which is the metal generally used for the binding posts on galvanometers and potentiometers. Thus, any stray thermoelectric potential caused by temperature differences between the contacts of the thermocouple wires with the binding posts is eliminated. The thermoelectric potential of a cooper – constantan couple with the reference junction at 0^0 C has a temperature coefficient which varies from about 20 $\mu V\ deg^{-1}$ at -200^0 C to 60 at 300^0 C. At room temperature, it is 43 $\mu V\ deg^{-1}$. This couple cannot be used for long above 500^0 C.

Another commonly used couple is Chromel P and Alumel, these two being iron-nickel alloys containing chromium and aluminum, respectively. The coefficient is about 40 $\mu V\ deg^{-1}$ over a very wide range. This thermocouple can be used at temperatures as high as 1300^0 C. *Iron – constantan*, with a somewhat higher coefficient (53 $\mu V\ deg^{-1}$ at room temperature), can be used to nearly 1000^0 C. Platinum together with an alloy of 10 percent rhodium in platinum has a small coefficient (6 $\mu V\ deg^{-1}$ at room temperature), but can be used as high as 1700^0 C.

In our laboratory we use a Pt – Pt (Rh) thermocouple.

In very rough work with large – gauge thermocouple wires the thermoelectric emf can be measured directly with a milivoltmeter or galvanometer possessing an internal resistance large in comparison with the thermocouple wires.

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TEMPERATURE CONTROL

As most of the properties studied in physical chemistry are affected by temperature, it is very important to have means whereby experiments can be carried out at constant temperature. Constant temperature baths, or ***thermostats***, are therefore an essential part of the equipment of a laboratory for physical chemistry.

Heated thermostat baths with automatic temperature control are more versatile and are indispensable when a constant temperature must be maintained over a long period.

The usual components of a thermostat are shown diagrammatically in figure 2.

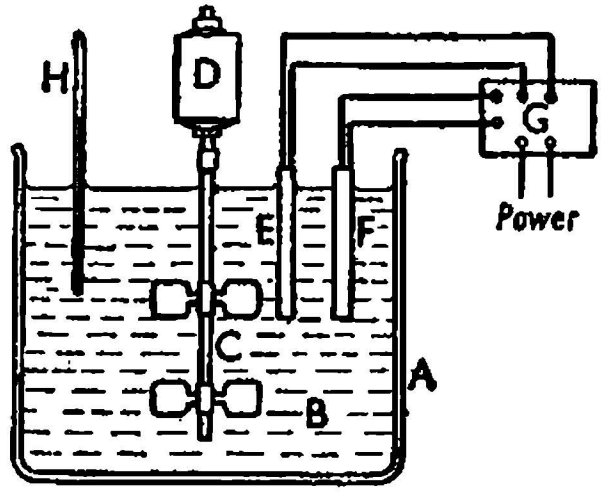

Figure 2. Components of a constant temperature bath (schematic)

A-tank, B-bath liquid, C-stirrer, D-electric motor, E-heater, F-thermoregulator, G-relay, H-thermometer

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I. THE DEVIATION QUANTITES FROM THE IDEAL BEHAVIOR

Thermodynamic characterization of macroscopic systems cannot be finalized without taking into account the report to a reference state. Consequently, the calculated quantities do not have an absolute meaning, but they are expressed as difference between thermodynamic property of the real system and that of ideal reference.

In the case of solutions, the reference state is ***the ideal solution***, and in the case of gases is ***the model of ideal gas***.

Intermolecular forces that act between the molecules of the systems can explain this approach which is specific to thermodynamics.

The dispersion forces able to interact between all types of molecules are the only one can act between non-polar molecules. The orientation and induction forces are specific for systems with polar and polar in interaction with non-polar molecules. The repulsive forces act at small separation and count only at extreme conditions – for example at high pressure.

The existence of intermolecular forces implies the introduction of partial molar quantities and other deviation functions in the thermodynamic treats of mixtures. The introduction of partial molar Gibbs free energy, in other words of chemical potential, allowed to Gibbs to define the specific thermodynamic investigation method – the thermodynamic and chemical potentials method.

I. a. PARTIAL MOLAR QUANTITIES

Equations expressing the change in properties with a change in composition are widely used in thermodynamics of solutions. Therefore, partial molar quantities play the same role in the thermodynamics of solutions as molar quantities in the thermodynamics of pure substances.

A general examination of the properties of a system, and of the variables that might be used to characterize those properties, discloses that they fall into two distinct classes, to be designated ***intensive*** and ***extensive***.

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An ***intensive*** variable of a homogeneous system is one whose magnitude is simultaneously characteristic both of the whole system and of any arbitrarily chosen macroscopic portion of it. An intensive variable measures an inherent property of a system, a property whose value does not depend on the size of the system. Pressure and temperature, for example, are intensive properties, for the same values can be used to describe either the entire system or any part of it.

The variables that have magnitudes proportional to the total amount of material under consideration, and other properties associated with them, are said to be ***extensive***; examples are mass, volume, energy, heat capacity and entropy. Defined precisely, an extensive property is a homogeneous function of first degree in the masses of materials present, such homogeneity being fulfilled while all intensive variables are held constant.

Instead of identifying an extensive property as one that is homogeneous with respect to masses, we can equally well say that it is homogeneous with respect to the numbers of moles of material present, for the mass of any substance is directly proportional to its number of moles, the proportionality factor being the molecular weight, a constant. In this connection we recognize that masses and numbers of moles are themselves extensive properties. Bearing in mind that one set of independent variables might be replaced by another set, we can now assert, as a conclusion, that an extensive property will exhibit homogeneity of first degree with respect to any and all extensive variables that are actually used for specifying the function. This permits us to select our independent variables to suit our convenience, without jeopardizing application of the homogeneity condition.

Lets consider an extensive property of a system – **Y** – (it could be the volume, the energy, the enthalpy, the heat capacity etc), which is dependent on the state parameters and composition.

$$\mathbf{Y} = \mathbf{Y}(T, P, n_1, n_2, ...n_i) \tag{I.1}$$

The elementary variation of this quantity, determined by the infinitezimal variation of the system composition is:

$$d\mathbf{Y} = \left(\frac{\partial \mathbf{Y}}{\partial n_1}\right)_{T,P,n_2,.....n_i} dn_1 + \left(\frac{\partial \mathbf{Y}}{\partial n_2}\right)_{T,P,n_1,n_2,.....n_i} dn_2 + ... + \left(\frac{\partial \mathbf{Y}}{\partial n_i}\right)_{T,P,n_1,.....n_{i-1}} dn_i \tag{I.2}$$

The considered state parameters are constant.

G. N. Lewis defined the ***partial molar quantities*** $\overline{Y_i}$ of the ith component as a partial derivative of **Y** with the number of moles n_i, at constant state parameters and constant composition:

$$\overline{Y_i} = \left(\frac{\partial \mathbf{Y}}{\partial n_i}\right)_{T,P,n_j \neq n_i} \tag{I.3}$$

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So, $\overline{Y_i}$ represents the rate of change of **Y** with respect to addition of substance i, will equal the increase in **Y** attending the addition of one mole of substance i to an infinite amount of system.

To illustrate how different properties can depend explicitly on different numbers of extensive variables, let us consider the example afforded by volume. To specify the volume of a system, we naturally choose as independent variables the temperature, the pressure, and the numbers of moles.

$$\mathbf{V} = \mathbf{V}(T, P, n_1, n_2, ...n_i) \tag{I.4}$$

The elementary variation of this quantity, determined by the infinitezimal variation of the system composition is:

$$d\mathbf{V} = \left(\frac{\partial \mathbf{V}}{\partial n_1}\right)_{T,P,n_2,....n_i} dn_1 + \left(\frac{\partial \mathbf{V}}{\partial n_2}\right)_{T,P,n_1,n_2,....n_i} dn_2 + ... + \left(\frac{\partial \mathbf{V}}{\partial n_i}\right)_{T,P,n_1,....n_{i-1}} dn_i \tag{I.5}$$

The expression of partial molar volume is:

$$\overline{V_i} = \left(\frac{\partial \mathbf{V}}{\partial n_i}\right)_{T,P,n_j \neq n_i} \tag{I.6}$$

Introducing equation (I.6) in equation (I.5) it can be obtain:

$$d\mathbf{V} = \overline{V_1} \cdot dn_1 + \overline{V_2} \cdot dn_2 + ... + \overline{V_i} \cdot dn_i \tag{I.7}$$

or: $$(d\mathbf{V})_{T,P} = \sum_i \overline{V_i} \cdot dn_i \tag{I.8}$$

We can express the partial molar quantity even like this:

$$\lim_{\Delta n_i \to 0} \left(\frac{\Delta \mathbf{V}}{\Delta n_i}\right)_{T,P,n_j \equiv n_i} = \overline{V_i} \tag{I.9}$$

The partial molar volume $\overline{V_i}$ will be precisely equal to the increase in volume of a solution when one mole of i^{th} component is added to an infinite volume of the solution.

In order to establish the fundamental equations of partial molar quantities we can use Euler's theorem on homogeneous functions. For a function of n^{th} degree and under considerations that homogeneity degree is equal to unity the Euler's theorem can be write:

$$x_1 \cdot \frac{\partial f}{\partial x_1} + x_2 \cdot \frac{\partial f}{\partial x_2} + ... + x_i \cdot \frac{\partial f}{\partial x_i} = n \cdot f(x_1, x_2, ...x_i) \tag{I.10}$$

If the theorem is applied to an extensive property of a thermodynamic system, such as the volume, it follows:

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$$\mathbf{V} = n_1 \cdot \left(\frac{\partial \mathbf{V}}{\partial n_1}\right)_{T,P,n_2,\ldots n_i} + n_2 \cdot \left(\frac{\partial \mathbf{V}}{\partial n_2}\right)_{T,P,n_1,n_2,\ldots n_i} + \ldots + n_i \cdot \left(\frac{\partial \mathbf{V}}{\partial n_i}\right)_{T,P,n_1,\ldots n_{i-1}}$$

$$\mathbf{V} = \sum_i n_i \cdot \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_1,n_2,\ldots n_i} = \sum_i n_i \cdot \overline{V}_i \qquad \text{Gibbs equation} \qquad \text{(I.11)}$$

Differentiating equation (I.11):

$$d\mathbf{V} = n_1 \cdot \frac{\partial \overline{V}_1}{\partial n_1} + \overline{V}_1 \cdot dn_1 + n_2 \cdot \frac{\partial \overline{V}_2}{\partial n_2} + \overline{V}_2 \cdot dn_2 + \ldots + n_i \cdot \frac{\partial \overline{V}_i}{\partial n_i} + \overline{V}_i \cdot dn_i =$$

$$\overline{V}_1 \cdot dn_1 + \overline{V}_2 \cdot dn_2 + \ldots + \overline{V}_i \cdot dn_i + n_1 \cdot \frac{\partial \overline{V}_1}{\partial n_1} + n_2 \cdot \frac{\partial \overline{V}_2}{\partial n_2} + \ldots + n_i \cdot \frac{\partial \overline{V}_i}{\partial n_i} \qquad \text{(I.12)}$$

Comparing equation (I.12) with equation (I.5) we can see that:

$$n_1 \cdot \frac{\partial \overline{V}_1}{\partial n_1} + n_2 \cdot \frac{\partial \overline{V}_2}{\partial n_2} + \ldots + n_i \cdot \frac{\partial \overline{V}_i}{\partial n_i} = 0 \qquad \text{or} \qquad \sum_{i=1}^{n} n_i \cdot \frac{\partial \overline{V}_i}{\partial n_i} = 0$$

$$\sum_{i=1}^{n} n_i \cdot d\overline{V}_i = 0 \qquad \text{Gibbs – Duhem equation} \qquad \text{(I.13)}$$

To determine partial molar volumes experimentally, we must measure volumes or densities of mixtures over a range of concentrations. We can than analyze the data so obtained graphically or otherwise to establish values for the appropriate partial derivatives. If empirical formulas are available for relating densities to concentrations, we can readily compute partial molar volumes by analytical methods.

In chapter of applications is presented an experimental method for the determination of partial molar volumes.

I. b. THE COMPRESSIBILITY FACTOR

The thermodynamic properties of an ideal gas (V, S, F, G, C_P, C_V) are established by using the ideal state equation, $PV = RT$. This equation is founded on simplified hypothesis according to the ideal gas posses only thermal energy, the molecular interaction energy being zero. The ideal gases posses a proper molecular volume but it is negligible in respect with the total occupied volume.

Because the real gases don't respect this simplified hypothesis, equation of state must contain quantities, which relate the intermolecular interaction and the real volume of molecules.

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The deviation of real gases from the ideal behavior can be characterized by the ***compressibility factor***, Z.

$$Z = \frac{PV}{RT} \qquad \text{(I.14)}$$

In a Z = f (P) graphical representation we remark the fact that when P→0, the isothermal curves converge to ideal gas state (Z = 1). At lower temperatures these curves present a minimum in the domain of low pressures. At pressures at which Z < 1, the volume of real gas is smaller that those of ideal gas at the same pressure. As a consequence, the gas is more compressible. For Z > 1 one observe a reduced compressibility of the real gas in comparison with ideal gas. In the domain when Z < 1, the intermolecular forces lead to the increasing of the real gas compressibility and in the domain where Z > 1, the proper volume of molecules contributes at the decreasing of gas compressibility. Together with rising of temperature the Z minimum is less marked and is displaced to smaller values of pressure. The temperature at which the curve Z = f (P) becomes tangent at ideal gas isotherm, for a wide range of pressure, is called Boyle temperature, T_B. At this temperature the real gas has an ideal behavior (Z = 1). Above Boyle curve, the curves Z = f (P) do not show a minimum, Z > 1, for any values P ≠ 0, and the deviations from ideal behavior decreases with increasing of temperature (see figure I.1).

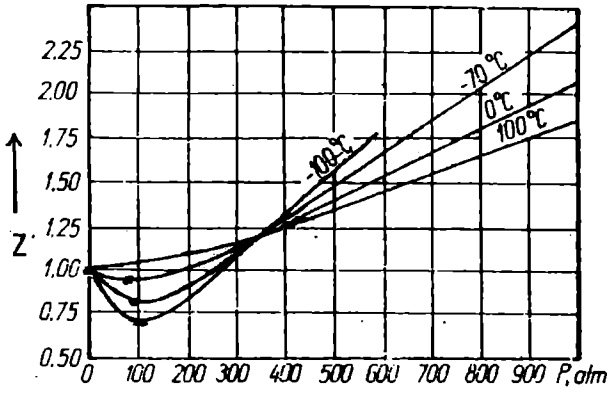

Figure I. 1 Pressure dependence of compressibility factor

It is often impossible to use the method of calculating the properties of a real gas, or vapors, because the required data are absent. The knowledge of compressibility factors makes easier this calculation; for example the calculation of fugacity coefficients may be realized by using of general thermodynamic equations:

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$$RT\ln\left(\frac{f}{P}\right)_{pure\ i} = \int_0^P \left(V_i - \frac{RT}{P}\right)dP = \int_0^P \frac{Z-1}{P}dP \qquad \text{(I.15)}$$

$$RT\ln(\gamma_i)_P = RT\ln\frac{f_i}{P_i} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,P,n_j} - \frac{RT}{V}\right]dV - RT\ln Z \qquad \text{(I.16)}$$

A generalized method of calculation is based on the principle of the corresponding states. According to this principle, the same common function:

$$f\left(\frac{P}{P_c},\frac{V}{V_c},\frac{T}{T_c}\right) = 0 \qquad \text{or} \qquad f(P_r,V_r,T_r) = 0 \qquad \text{(I.17)}$$

exists for all substances. In other words, if instead of expressing the properties of gases (liquids) through P, V and T, we use dimensionless units for this purpose – the ***reduced parameters***, P_r, V_r, T_r, then we can obtain a reduced equation (I.17) which contains none of the quantities characterizing a given substance. Such an equation can be obtain from any equation of state having three constants (for example: van der Waals equation).

The application of the principle of corresponding states makes it possible to use values of P_r and T_r, resorting when necessary to the properties of a gas at P = 1 atm, to calculate various properties of gases within a broad range of temperatures and pressures. It is often good to perform the calculations with graphs plotted on the basis of equations relating a given property of a gas to the reduced parameters. Considering that all gases in the corresponding states have about the same compression factors, the calculations can be perform with the aid of a graph $Z = f(P_r, T_r)$, where this function is a universal function of the reduced parameters. We can approximate the application of the principle of corresponding state and consequently the use of the graph $Z = f(P_r, T_r)$ when the value of critical compressibility factor $Z_c = \frac{P_c \cdot V_c}{R \cdot T_c} \cong 0.3$.

In chapter of applications is presented an experimental method for the determination of compressibility factors.

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II. FUNDAMENTAL NOTIONS OF CALORIMETRY

In this chapter we are concerned with the problem of determining experimentally the enthalpy change ΔH or the energy change accompanying a given isothermal change in state of a system, normally one in which a chemical reaction occurs. We can write the reaction schematically in the form:

$$\nu_1 A_1(T_0) + \nu_2 A_2(T_0) + ... = \nu_1' A_1'(T_0) + \nu_2' A_2'(T_0) + ... \qquad \text{(II.1)}$$

initial state final state

In practice we do not actually carry out the change in state isothermally; this is not necessary because ΔH and ΔE are independent of the path. In calorimetry we usually find it convenient to use a path composed of two steps:

Step I: A change in state is carried out *adiabatically* in the calorimeter vessel to yield the desired products but in general at another temperature:

$$\nu_1 A_1(T_0) + \nu_2 A_2(T_0) + ... + A_c(T_0) = \nu_1' A_1'(T_1) + \nu_2' A_2'(T_1) + ... + A_c(T_1) \qquad \text{(II.2)}$$

where A_c represents those parts of the system (e.g., inside wall of the calorimeter vessel, stirrer, thermometer, solvent) that are always at the same temperature as the reactants or products because of the experimental arrangement; these parts, plus the reactants or products, constitute the system under discussion.

Step II: The products of step I are brought to the initial temperature T_0 by adding the heat to (or taking it from) the system:

$$\nu_1' A_1'(T_1) + \nu_2' A_2'(T_1) + ... + A_c(T_1) = \nu_1' A_1'(T_0) + \nu_2' A_2'(T_0) + ... + A_c(T_0) \qquad \text{(II.3)}$$

By adding equation (II.2) and (II.3) we obtain equation (II.1) and verify that these two steps describe a complete path connecting the desired initial and final states. Accordingly, ΔH or ΔE for the change in state (1) is the sum of the values of this quantity pertaining the two steps:

$$\Delta H = \Delta H_I + \Delta H_{II} \qquad \text{(II.4a)}$$

$$\Delta E = \Delta E_I + \Delta E_{II} \qquad \text{(II.4b)}$$

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The particular convenience of the path described is that the heat Q for step I is zero, while the heat Q for step II can be either measured or calculated. It can be measured directly by carrying out step II (or its inverse) through the addition to the system of a measurable quantity of heat or electrical energy, or it can be calculated from the temperature change ($T_1 - T_0$) resulting from adiabatic step I if the heat capacity of the product system is known. For step I,

$$\Delta H_I = Q_P = 0 \qquad \text{constant pressure} \qquad \text{(II.5a)}$$

$$\Delta E_I = Q_V = 0 \qquad \text{constant volume} \qquad \text{(II.5b)}$$

Thus, if *both* steps are carried out at constant pressure,

$$\Delta H = \Delta H_{II} \qquad \text{(II.6a)}$$

and if *both* are carried out at constant volume,

$$\Delta E = \Delta E_{II} \qquad \text{(II.6b)}$$

In nearly all cases it is most convenient to carry it out at constant pressure; the experiments on heats of ionic reaction and heats of solution are examples. An exception to the general rule is the determination of a heat of combustion, which is conveniently carried out at constant volume in a bomb. However, we can easily calculate ΔH from ΔE as determined from a constant-volume process (or ΔE from ΔH as determined from a constant-pressure process) by use of the equation:

$$(\Delta H)_{T,P} = (\Delta E)_{T,V} + P\Delta V \qquad \text{(II.7)}$$

When all reactants and products are condensed phases, the PΔV term is negligible in comparison with ΔH or ΔE, and the distinction between these two quantities is unimportant. When gases are involved, as in the case of combustion, the PΔV term is likely to be significant in magnitude, though still small, in comparison with ΔH or ΔE. since it is small, we can employ the perfect-gas law and rewrite equation (II.7) in the form:

$$(\Delta H)_{T,P} = (\Delta E)_{T,V} + RT\Delta\nu_{gas} \qquad \text{(II.8)}$$

where $\Delta\nu_{gas}$ is the *increase* in the number of moles of gas in the system.

If we know or can determine the heat capacity of the system, the temperature change ($T_1 - T_0$) resulting from the step I provides all the additional information we need:

$$\Delta H_{II} = \int_{T_1}^{T_0} C_p \left(\nu_1' A_1' + \nu_2' A_2' + \ldots + A_c\right) dT \qquad \text{(II.9a)}$$

$$\Delta E_{II} = \int_{T_1}^{T_0} C_v \left(\nu_1' A_1' + \nu_2' A_2' + \ldots + A_c\right) dT \qquad \text{(II.9b)}$$

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The heat capacities ordinarily vary only slightly over the small temperature ranges involved; accordingly we can write:

$$\Delta H_{II} = C_p\left(\nu_1' A_1' + \nu_2' A_2' + ... + A_c\right)\cdot\left(T_0 - T_1\right) \qquad \text{(II.10a)}$$

$$\Delta E_{II} = C_v\left(\nu_1' A_1' + \nu_2' A_2' + ... + A_c\right)\cdot\left(T_0 - T_1\right) \qquad \text{(II.10b)}$$

where C_P and C_V are average values over the temperature range or to a good approximation may be regarded as constants independent of temperature.

The heat capacity of the system, if not known, must be determined.

- A direct method, which depends on the assumption of the constancy of heat capacities over a small range of temperature, is to measure the temperature rise ($\Delta T_1 = T_1 - T_0$) produced by the dissipation of a measured quantity of electrical energy;
- An indirect method of determining the heat capacity is to carry out another reaction altogether, for which the heat of reaction is known, in the same calorimeter under the same conditions.

Let us now consider the adiabatic step, step I, and the measurement of the temperature difference ($T_1 - T_0$) which is fundamental measurement of calorimetry. It is an idealization to assume that step I is truly adiabatic. As no thermal insulation is perfect, some heat will in general leak into or out of the system during the time required for the change in state to occur and for the thermometer to come into equilibrium with the product system.

In addition, we usually have a stirrer present in the calorimeter to aid in the mixing of reactants or for hastening thermal equilibration the mechanical work done on the system by the stirrer results in the continuous addition of energy to the system at a small, approximately constant rate. During the time required for the change in state and thermal equilibration to occur, the amount of energy introduced can easily be significant.

The following are the most important experimental approaches aimed at minimizing the effect of non-adiabatic conditions and the effect of the stirrer:

- The calorimeter may be built in such a way as to minimize heat conduction in or out of the system. A vessel with an evacuated jacket (Dewar flask), often with silvered surfaces to minimize the effect of heat radiation, may be used.
- The stirring system may be carefully designed to produce the least rate of work consistent with the requirement of thorough and reasonably rapid mixing.
- We may assume that the rate of gain or loss of energy by the system resulting from heat leak and stirrer work is reasonably constant with time at any given temperature. We may therefore assume that the temperature, as a function of time, should be initially and finally linear. Thus we can

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estimate what the temperature T_1 would be in the event of instant equilibration by plotting temperature against time for a period long enough to obtain a curve with a long portion that is essentially linear and extrapolating this linear portion back to the time of initiation of the reaction, as shown in figure 3. Where the time required for the change in state is long, as in the case of determining the heat capacity by electrical heating, the rate of heat leak presumably changes continuously from the initiation of electrical heating to its termination, and it would be improper to extrapolate to the time of initiation of the heating. The appropriate procedure in this case would be to extrapolate the linear portions of the heating curves for the periods before initiation and after termination to the middle of the heating period.

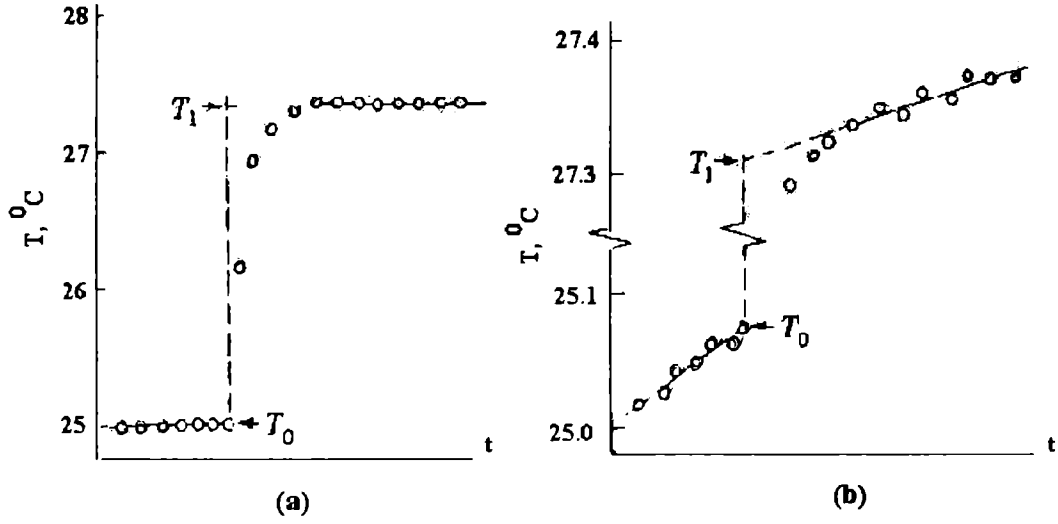

Figure II.1

(a) Schematic plot of temperature T versus time t showing the extrapolation for obtaining T_1

(b) Plot with interrupted temperature axis and greatly expanded temperature scale. Such plot will eliminate the contribution of graphical errors to the uncertainty in $T_1 - T_0$.

As applications in this chapter we will present the following experimental works:

- Enthaplies of reactions. Application of Hess's Law;
- Heat of vaporization;
- Heat of combustion.

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III. CHEMICAL EQUILIBRIUM

The concept of equilibrium is fundamental for the understanding of any physical and chemical process. Systems in equilibrium are those that not change their state as long as an external factor don't act on them. Chemical equilibrium don't suppose a state of absolute repose but on the contrary it is a dynamic equilibrium, the direct and inverse transformations taking place simultaneously and with the same rate so that from the macroscopic point of view nothing can be observed.

Chemical equilibrium is based on reversibility of reaction and some temperature, pressure and concentration conditions when obtaining a "stationary" mixture that contains also the reactants and reaction products.

There are two different ways by which the chemical equilibrium can be treated using the methods of kinetics and thermodynamics. By kinetics method, the chemical equilibrium treaties the rate and the mechanism of the reaction. From thermodynamics point of view, the chemical equilibrium is treated in connection with variation of chemical affinity, which accompanied the reaction, without taking into account the path and rate.

The study of chemical equilibrium, characterized by equilibrium constant calculus, represents the main problem of chemical thermodynamics. Called as affinity constant $\left(A = -\Delta G^0 = RT \ln K\right)$, its calculation is correlated with possibilities of evaluation of standard Gibbs free energy.

III. a. Calculation of the free energy of a reaction

Let consider a chemical reaction:

$$\nu_1 A_1 + \nu_2 A_2 + ... + \nu_i A_i \Leftrightarrow \nu_1' A_1' + \nu_2' A_2' + ... \nu_i' A_i' \qquad \text{(III.1)}$$

At time t = 0	n_1^0	n_2^0 ...	n_i^0	0	0	0	moles number
Free energies of pure reactants	G_1	G_2 ...	G_i				
At time t	n_1	n_2 ...	n_i	n_1'	n_2'...	n_i'	moles number
At an infinitezimal							

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Variation, dt	$-dn_1$	$-dn_2$...	$-dn_i$	dn_1'	dn_2'...	dn_i'
Partial molar free energies	$\overline{G}_1$	$\overline{G}_2$...	$\overline{G}_i$	$\overline{G}_1'$	$\overline{G}_2'$...	$\overline{G}_i'$

For an infinitezimal process, free energy of reaction will be:

$$dG_{T,P} = \overline{G}_1' dn_1' + \overline{G}_2' dn_2' + ... + \overline{G}_i' dn_i' + \overline{G}_1(-dn_1) + \overline{G}_2(-dn_2) + ... + \overline{G}_i(-dn_i)$$
$$dG_{T,P} = \sum_i \overline{G}_i' dn_i' - \sum_i \overline{G}_i dn_i \qquad \text{(III.2)}$$

Variations of mole numbers are determined by the stoechiometry of the process:

$$-\frac{dn_1}{\nu_1} = -\frac{dn_2}{\nu_2} = ... = -\frac{dn_i}{\nu_i} = \frac{dn_1'}{\nu_1'} = \frac{dn_2'}{\nu_2'} = ... = \frac{dn_i'}{\nu_i'} = d\lambda \qquad \text{(III.3)}$$

where λ is called ***advance degree of reaction*** and belongs to the interval $\lambda \in [0,1]$; λ = 0 at the initial time of the process and λ = 1 at the end of the process (in the case of a total reaction).

Knowing the meaning of the term $\frac{dn_i}{\nu_i}$, equation (III.2) will became:

$$dG_{T,P} = \left(\sum_i \nu_i' \overline{G}_i' - \sum_i \nu_i \overline{G}_i \right) \cdot d\lambda \qquad \text{(III.4)}$$

Free energy ΔG is defined by the ratio:

$$\left(\frac{dG}{d\lambda} \right)_{T,P} = \Delta G_{T,P} = \sum_i \nu_i' \overline{G}_i' - \sum_i \nu_i \overline{G}_i \qquad \text{(III.5)}$$

In the case when $\Delta G = \Delta G^0$, standard free energy of the reaction can be calculated from standard free energy of formation:

$$\Delta G^0 = \sum_i \nu_i' \left(\Delta G_i^0 \right)_f' - \sum_i \nu_i \left(\Delta G_i^0 \right)_f \qquad \text{(III.6)}$$

The values of standard free energy of reaction can be calculated by using standard enthalpies and entropies of formation:

$$\Delta G_{T,P}^0 = \Delta H^0 - T \cdot \Delta S^0 = \left[\sum_i \nu_i' \left(H_f^0 \right)_i' - \sum_i \nu_i \left(H_f^0 \right)_i \right] - T \cdot \left[\sum_i \nu_i' \left(S_f^0 \right)_i' - \sum_i \nu_i \left(S_f^0 \right)_i \right] \qquad \text{(III.7)}$$

Correlation of free energy and chemical potential is given by the equation:

$$\left(\frac{dG}{d\lambda} \right)_{T,P} = \Delta G_{T,P} = \sum_i \nu_i' \mu_i' - \sum_i \nu_i \mu_i \qquad \text{(III.8)}$$

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$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \overline{G}_i = \mu_i$ for non-ideal system and $\overline{G}_i = G_i = \mu_i$ for an ideal system.

The expression of chemical potential for a component of a system with ideal behavior is:

$$\mu_i = G_i = \mu_i^0 + RT \ln x_i \qquad \text{(III.9)}$$

where μ_i^0 is standard chemical potential and x_i is molar fraction of i[th] component , relation (III.8) will become:

$$\Delta G_{T,P} = \left(\sum_i \nu_i' \mu_i^{0'} - \sum_i \nu_i \mu_i^0\right) + RT \cdot \left(\sum_i \nu_i' \ln x_i' - \sum_i \nu_i \ln x_i\right) \Rightarrow$$

$$\Delta G_{T,P} = \Delta G^0 + RT \cdot \ln \frac{\prod_i x_i'^{\nu_i'}}{\prod_i x_i^{\nu_i}} \qquad \text{(III.10)}$$

where $\Delta G^0 = \sum_i \nu_i' \mu_i^{0'} - \sum_i \nu_i \mu_i^0$ represents standard free energy of the reaction.

In most cases there are confusions in understanding the physical meaning of this two functions ΔG and ΔG^0. ΔG represents the variation of free energy associated to a chemical process in certain conditions and at equilibrium $(\Delta G)_{T,P} = 0$. ΔG^0 represents the standard free energy of reaction, defined at standard conditions and it can never be canceled.

At chemical equilibrium:

$$(\Delta G)_{T,P} = 0 \Rightarrow \Delta G^0 + RT \cdot \ln \frac{\prod_i x_i'^{\nu_i'}}{\prod_i x_i^{\nu_i}} = 0 \qquad \text{(III.11)}$$

$$\frac{\prod_i x_i'^{\nu_i'}}{\prod_i x_i^{\nu_i}} = \frac{x_1'^{\nu_1'} \cdot x_2'^{\nu_2'} \cdot \ldots \cdot x_i'^{\nu_i'}}{x_1^{\nu_1} \cdot x_1^{\nu_1} \cdot \ldots \cdot x_i^{\nu_i}} = K_{x_{(T,P)}} \qquad \text{(III.12)}$$

The above relation represents the law of mass action or chemical equilibrium law (Guldberg and Waage). This law shows that the radio between the products of the concentrations of bodies resulted from the reaction at a power equal to the stoechiometric coefficients and the product of the reactants concentrations at a power equal to the stoechiometric coefficients define the equilibrium constant which is dependent on the temperature and the pressure associated to the reaction.

Combining the equation (III.12) with equation (III.11) one can obtain:

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$$\Delta G^0 = -RT \cdot \ln K_x \qquad \text{(III.13)}$$

In general case:

$$\Delta G_{T,P} = -RT \cdot \ln K_x + RT \cdot \ln \frac{\prod_i x_i'^{\nu_i'}}{\prod_i x_i^{\nu_i}} = 0 \qquad \text{(III.14)}$$

K_x is called ***thermodynamic equilibrium constant***.

Should be specified that the established thermodynamic relations, which are correct from the thermodynamic point of view, have a limited validity because of the simplified form of chemical potential (III.9).

The true thermodynamic equilibrium constant can be obtained by substituting molar fractions x_i with thermodynamic activities:

$$a_i = x_i \cdot \gamma_i \qquad \text{(III.15)}$$

where γ_i is a activity coefficient and has a meaning of a correction factor (it can be calculated by specific thermodynamic methods depending on structure of the system) which take into account the interaction forces that act between the molecules.

$$\mu_i = \mu_i^{\bullet}(T,P) + RT \ln a_i \qquad \text{(III.16)}$$

where $\mu_i^{\bullet}(T,P)$ is the standard chemical potential in non-ideal system.

In the case when some reactants or products of reaction are real gases the expression of chemical potential is:

$$\mu_i = \mu_i^{\bullet}(T) + RT \ln f_i \qquad \text{(III.17)}$$

where $f_i = P_i \cdot (\gamma_i)_P$ defines the fugacity of ith component, and $(\gamma_i)_P$ - the fugacity coefficient can be calculated from thermodynamic relations:

$$RT \ln\left(\frac{f}{P}\right)_{pure\ i} = \int_0^P \left(V_i - \frac{RT}{P}\right) dP; \qquad \ln\left(\frac{f}{P}\right)_{pure\ i} = \ln \gamma_i = \int_0^P \frac{Z-1}{P} dP \qquad \text{(III.18)}$$

where V_i and Z represent the molar volume and the compressibility factor of pure i, respectively.

In the case of a mixture, the fugacity coefficient of ith component can be calculated from the relation:

$$RT \ln(\gamma_i)_P = RT \ln \frac{f_i}{P_i} = \int_V^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,P,n_j} - \frac{RT}{V} \right] dV - RT \ln Z \qquad \text{(III.19)}$$

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In this case $Z = \frac{PV}{RT}$ is the compressibility factor of the mixture. The compressibility factor Z can be calculated by using of an appropriate equation of state or it can be obtained from experimental data by using Burnett method.

Equation (III. 10) will become:

$$\Delta G_{T,P} = \Delta G^0 + RT \cdot \ln \frac{\prod_i a_i^{'\nu_i}}{\prod_i a_i^{\nu_i}} \qquad \text{(III.20)}$$

where: $$\frac{\prod_i a_i^{'\nu_i}}{\prod_i a_i^{\nu_i}} = \frac{a_1^{'\nu_1} \cdot a_2^{'\nu_2} \cdot \ldots \cdot a_i^{'\nu_i}}{a_1^{\nu_1} \cdot a_1^{\nu_1} \cdot \ldots \cdot a_i^{\nu_i}} = K_{a_{(T,P)}} \qquad \text{(III.21)}$$

K_a is the ***true thermodynamic equilibrium constant***.

In order that equation (III.17) is valid it is necessary that values of ΔG^0 and a have to correspond to identical standard states. Otherwise this equation leads to important errors.

III. b. Different forms of equilibrium constants

$$K_x = \frac{x_1^{'\nu_1} \cdot x_2^{'\nu_2} \cdot \ldots \cdot x_i^{'\nu_i}}{x_1^{\nu_1} \cdot x_1^{\nu_1} \cdot \ldots \cdot x_i^{\nu_i}}; \quad K_P = \frac{P_1^{'\nu_1} \cdot P_2^{'\nu_2} \cdot \ldots \cdot P_i^{'\nu_i}}{P_1^{\nu_1} \cdot P_1^{\nu_1} \cdot \ldots \cdot P_i^{\nu_i}}; \quad K_c = \frac{c_1^{'\nu_1} \cdot c_2^{'\nu_2} \cdot \ldots \cdot c_i^{'\nu_i}}{c_1^{\nu_1} \cdot c_1^{\nu_1} \cdot \ldots \cdot c_i^{\nu_i}} \qquad \text{(III.22)}$$

The following relation correlates these tree forms of equilibrium constants:

$$K_x = K_P \cdot P^{\Delta\nu} = K_c \cdot \left(\frac{RT}{P}\right)^{\Delta\nu} \qquad \text{(III.23)}$$

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III. c. Laws of chemical equilibrium displacement

(Principle of mobile equilibrium Le Chatelier – Braun)

- Temperature dependence of chemical equilibrium:

Starting from the relation $\Delta G^0 = -RT \ln K_x$ and Gibbs-Helmholtz equation

$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$ we can write:

$$\frac{d \ln K_x}{dT} = -\frac{1}{R}\left[\frac{d\left(\Delta G^0/T\right)}{dT}\right]_P = \frac{\Delta H^0}{RT^2} \qquad \text{(III.24)}$$

ΔG^0 and ΔH^0 are, respectively, the standard Gibbs free energy change and the standard enthalpy change. In the general case $\Delta H^0 = \Delta H$ and represents the enthalpy of reaction in specified condition of temperature and pressure.

From equation (III.24) results that an increase of temperature favors the endothermic reactions ($\Delta H > 0$) while a decrease of temperature favors the exothermic reactions ($\Delta H < 0$)

In the case of thermal decomposition of calcium carbonate: $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$

At 1 atm, $$K_x = K_P = \frac{a_{CaO(s)} \cdot a_{CO_2(g)}}{a_{CaCO_3(s)}} = a_{CO_2(g)} = f_{CO_2(g)} = P_{CO_2} \qquad \text{(III.25)}$$

because by convention, the activities of condensed phases are equal with unity. In this case the equation (III.24) becomes:

$$\frac{d \ln K_x}{dT} = \frac{d \ln K_P}{dT} = \frac{d \ln P_{CO_2}}{dT} = \frac{\Delta H}{RT^2} \qquad \text{(III.26)}$$

After integrating between two values of temperature and pressure (T_1, T_2; P_1, P_2):

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{dissoc}}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{(III.27)}$$

- Pressure dependence of chemical equilibrium

When the relation $\Delta G^0 = -RT \ln K_x$ is derived in respect with pressure, one obtains:

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$$\left(\frac{\partial \ln K_x}{\partial P}\right)_T = -\frac{1}{R}\frac{\partial}{\partial P}\left(\frac{\Delta G^0}{T}\right) = -\frac{\Delta V}{RT} \qquad \text{(III.28)}$$

This equation states that with an increase in pressure chemical equilibrium should shift in direction with ΔV.

As application of the general theory of chemical equilibrium we will study in our laboratory the following two experimental works:

- Thermal decomposition of calcium carbonate
- Chemical equilibrium in gases

III. d. Electrochemical equilibrium

When the dissociation process of a dissolved substance and the association of ions go on reversibly, the process respects the laws of chemical equilibrium. Ostwald considered a solution in which every component respects the laws of an ideal osmosis. Chemical potential μ_i of a component with molarity c can be write:

$$\mu_i = \mu_i^0 + RT \ln c_i \qquad \text{(III.29)}$$

Chemical potential μ_i^0 for concentration c = 1 mole l^{-1} depends on temperature and pressure. In the case of a uni-univalent electrolyte AB, which forms such a solution and dissociate by the equation:

$$AB \Leftrightarrow A^+ + B^- \qquad \text{(III.30)}$$

the following relation is respected:

$$\mu_{AB} = \mu_+ + \mu_- \qquad \text{(III.31)}$$

In this case, the law of mass action is written in the form:

$$\frac{c_+ c_-}{c_{AB}} = \exp\left[-\frac{\mu_+^0 + \mu_-^0 - \mu_{AB}}{RT}\right] = K(T,P) \qquad \text{(III.32)}$$

where c_+, c_- and c_{AB} are the equilibrium concentrations of the species: A^+, B^- and AB.

In the case when by c is noted the total concentration of dissolved substances:

$$\begin{aligned} c_A &= c_B = c \cdot \alpha \\ c_{AB} &= c \cdot (1 - \alpha) \end{aligned} \qquad \text{(III.33)}$$

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where α represents the dissociation degree of electrolyte AB.

Generally, the dissociation process can be written:

$$A_{\nu_-}^{z-}B_{\nu_+}^{z+} \Leftrightarrow \nu_- A^{z-} + \nu_+ B^{z+} \qquad \text{(III.34)}$$

where $\nu_- z^- = \nu_+ z^+$ and $\nu = \nu_+ + \nu_-$ represents the total number of ions.

For this process, the dissociation constant is:

$$K = \frac{(\alpha \cdot c \cdot \nu_+)^{\nu+} \cdot (\alpha \cdot c \cdot \nu_-)^{\nu-}}{c \cdot (1-\alpha)} = \frac{c^{\nu} \cdot \alpha^{\nu} \cdot {\nu_+}^{\nu+} \cdot {\nu_-}^{\nu-}}{c \cdot (1-\alpha)} \qquad \text{(III.35)}$$

with: $c_+ = \alpha \cdot c \cdot \nu_+$ and $c_- = \alpha \cdot c \cdot \nu_-$ are the concentration of positive and negative ions, and $c_{nondissoc} = c - \alpha \cdot c = c \cdot (1-\alpha)$

In the case of uni-univalent electrolyte:

$$K = \frac{\alpha^2 \cdot c^2}{c \cdot (1-\alpha)} = \frac{\alpha^2 \cdot c}{1-\alpha} \qquad \text{The Ostwald dilution Law} \qquad \text{(III.36)}$$

Because the dissociation degree α is defined as equal to the ratio between the equivalent conductivity of a solution at a concentration c and at infinite dilution: $\alpha = \frac{\Lambda}{\Lambda_\infty}$, the dissociation equilibrium constant K can be obtain by experimental measurements of conductivity.

$$K = \frac{\left(\frac{\Lambda}{\Lambda_\infty}\right)^2 \cdot c}{1 - \frac{\Lambda}{\Lambda_\infty}} \qquad \text{(III.37)}$$

As an application of electrochemical equilibrium we will study in the laboratory the dissociation process of a weak acid.

III. e. Heterogeneous chemical equilibrium between metals and electrolytes

It is known that all metals posses a higher or smaller capacity to send the ions in the solution. This capacity is called the electrolytic pressure of dissolution, P. The ions of the metal present in the solution are opposed against this pressure and as consequence are characterized by osmotic pressure, π. Function of these two effects, the metal will be charged (+) or (-), as follows:

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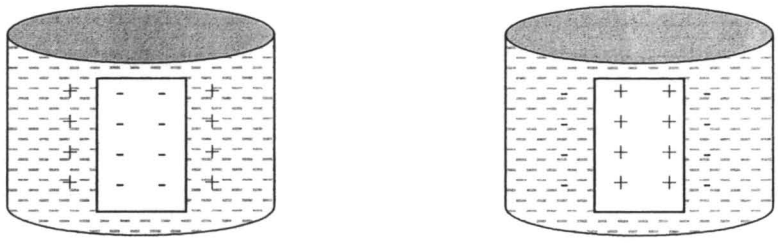
a) $P > \pi$, the metallic plate is charged negative because a number of ions passes in the solution: $M \rightarrow M^{+n} + ne^-$. These electrons remain in excess in the metal and will be charged negative the surface of the plate.

b) $P < \pi$, the metal is charged positive because some of the metal ions passes on the metallic surface (see figure III.1).



a) $P > \pi$ b) $P < \pi$

Figure III.1

Due to the transfer of the ions from a phase into another, at the interface metal – solution is formed a double electric layer characterized by an electromotive force. This layer is similar of a condenser, the potential difference between the armatures determine the potential of the metal in respect with the solution. The equilibrium of the two mentioned processes are realized when the difference of the chemical potential between the atoms in the metal and the ions in the solution balanced the difference of electric potential, ε. This potential difference at which the equilibrium is established is named the electrode potential.

The equilibrium condition is:

$$\Delta G = -n \cdot F \cdot \varepsilon \qquad \text{(III.38)}$$

When two electrodes are connected, they form a voltaic cell.

The electromotive force (emf) of a voltaic cell depends upon temperature. From the temperature coefficient of electromotive force and knowledge of emf at a particular temperature, three thermodynamic quantities, associated with the reversible reaction occurring in the cell, can be evaluated. These thermodynamic quantities are the free energy increase ΔG, the entropy increase ΔS and the enthalpy increase ΔH, given by the following equations:

- the free energy increase ΔG can be evaluated from the equation (III.38);
- by derivation of the equation (III.38) with T we obtain:

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$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -n \cdot F \cdot \left(\frac{\partial \varepsilon}{\partial T}\right)_P \qquad \text{(III.39)}$$

Knowing that:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \qquad \text{(III.40)}$$

- from equations (III.39) and (III.40) results:

$$\Delta S = n \cdot F \cdot \left(\frac{\partial \varepsilon}{\partial T}\right)_P \qquad \text{(III.41)}$$

- from equations (III.38), (III.39) and (III.41), the enthalpy will be:

$$\Delta H = \Delta G + T \cdot \Delta S = -n \cdot F \cdot \varepsilon + T \cdot n \cdot F \cdot \left(\frac{\partial \varepsilon}{\partial T}\right)_P = n \cdot F \cdot \left[T \cdot \left(\frac{\partial \varepsilon}{\partial T}\right)_P - \varepsilon\right] \qquad \text{(III.42)}$$

where ε is the emf of the cell, n is the number of electrons involved in the reaction, T is the absolute temperature and $\left(\partial\varepsilon/\partial T\right)_P$ is the temperature coefficient of the emf.

Calculation of thermodynamics functions: $\Delta G, \Delta H, \Delta S$ for a galvanic cell will be present as application of this theory.

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IV. PHASE EQUILIBRIA

In discussion the general subject of phase equilibria, we shall find it necessary to speak of the following three quantities:

- the number of phases – P;
- the number of components (or independent constituents) – C;
- the number of degrees of freedom, or variance – F.

Phase – by number of phases we shall mean the number of distinct kinds of homogeneous regions characterized by definite intensive properties and separated from one another by boundaries determined by discontinuities in one or more of this intensive properties.

Components – by number of components we shall mean the minimum number of pure chemical substances that are required for the preparation of arbitrary amounts of all the phases of the system. The number of components can be calculated by using of the following relation:

Number of components = number of chemical species – number of restriction conditions (stoechiometric relations, electroneutrality conditions, chemical equilibria).

Variance – by number of degrees of freedom – or variance, of a system at equilibrium, we shall mean the number of intensive variables that can arbitrarily change, within limits, without causing any phase to disappear or any new phase to appear.

Gibbs Phase Rule illustrates the connection between these three quantities.

$$F = C + 2 - P \qquad \text{(IV.1)}$$

IV. a. THE NERNST DISTRIBUTION LAW

Consider the two - phase liquid system consisting the two non-miscible or slightly miscible components α and β. If a third component soluble in both liquids (with different degree of solubility) is added, it is distributed between the two liquids, according the equilibrium:

$$C^{\alpha} \Leftrightarrow C^{\beta} \qquad \text{(IV.2)}$$

Equilibrium condition, chemical potential of C component is the same in each phase, is:

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$$\mu^{\alpha} = \mu^{\beta} \qquad \text{(IV.3)}$$

The chemical potentials are expressed in terms of their equilibrium molar concentrations by equations:

$$\mu_C^{\alpha} = \mu_C^{\bullet\alpha}(T,P) + RT\ln a_C^{\alpha} = \mu_C^{\bullet\alpha}(T,P) + RT\ln x_C^{\alpha}\cdot\gamma_C^{\alpha} \qquad \text{(IV.4)}$$

$$\mu_C^{\beta} = \mu_C^{\bullet\beta}(T,P) + RT\ln a_C^{\beta} = \mu_C^{\bullet\beta}(T,P) + RT\ln x_C^{\beta}\cdot\gamma_C^{\beta} \qquad \text{(IV.5)}$$

At equilibrium:

$$\Delta\mu_{T,P} = \mu^{\beta} - \mu^{\alpha} = 0 \Rightarrow \ln\frac{x_C^{\beta}\cdot\gamma_C^{\beta}}{x_C^{\alpha}\cdot\gamma_C^{\alpha}} = -\frac{\mu_C^{\bullet\beta} - \mu_C^{\bullet\alpha}}{RT} \Rightarrow K_{T,P} = \frac{x_C^{\beta}\cdot\gamma_C^{\beta}}{x_C^{\alpha}\cdot\gamma_C^{\alpha}} = \exp\left(-\frac{\mu_C^{\bullet\beta} - \mu_C^{\bullet\alpha}}{RT}\right) \qquad \text{(IV.6)}$$

where $K_{T,P}$ define the Nernst distribution constant.

For an ideal dilute solution, $\gamma = 1$, the Nernst distribution constant can be expressed by the ration between molar fractions or volumetric concentration:

$$K_{T,P} = \frac{x_C^{\beta}}{x_C^{\alpha}} = \frac{\dfrac{n_C^{\beta}}{n_C^{\alpha}+n_C^{\beta}}}{\dfrac{n_C^{\alpha}}{n_C^{\alpha}+n_C^{\beta}}} = \frac{n_C^{\beta}}{n_C^{\alpha}} = \frac{\dfrac{n_C^{\beta}}{V}}{\dfrac{n_C^{\alpha}}{V}} = \frac{c^{\beta}}{c^{\alpha}} \qquad \text{(IV.7)}$$

where c^{α} and c^{β} are the volumetric concentrations of C component in the two phases.

In an experimental work we will study the equilibrium, which arise when acetic acid is distributed between water and benzene.

IV. b. LIQUID – VAPOR EQUILIBRIUM

- ***One component system***

Let us consider the following vapor – liquid equilibrium:

$$C^{l} \Leftrightarrow C^{g} \qquad \text{(IV.8)}$$

The variations of Gibbs free energy for each phase will be:

$$dG^{g} = -S^{g}dT + V^{g}dP \qquad \text{(IV.9)}$$

$$dG^{l} = -S^{l}dT + V^{l}dP \qquad \text{(IV.10)}$$

In writing these equations, we assume that the temperature and pressure are the same for both phases, but that the other thermodynamic properties may be different. By subtracting the equation

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(IV.10) from (IV.9) we get the total difference of the change in Gibbs free energy for the evaporation process:

$$d\Delta G = -\Delta S dT + \Delta V dP \qquad \text{(IV.11)}$$

where $\Delta S = S^g - S^l$ and $\Delta V = V^g - V^l$. If we now stipulate that equilibrium is maintained both before and after the temperature and pressure have been changed, it follows that $d\Delta G = 0$.

After rearrangement we conclude that:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \cdot \Delta V} \qquad \text{(IV.12)}$$

This result, known as the ***Clapeyron equation***, is one of the most important equations of thermodynamics. It is applicable not merely to liquid – vapor equilibria but also to equilibria between solids and vapors, between solids and liquids, and between two solids modifications of a substance.

If we apply the Clapeyron equation to a liquid – vapor equilibrium, we can make several approximations that permit us to arrive at some simple but useful conclusions. We will neglect the volume of the liquid compared with that of the vapor ($\Delta V^g = V^g - V^l \cong V^g$). When we assume that the vapor behave as an ideal gas we can write that $V^g = {}^{RT}/_{P}$.

Upon introduction of this approximation into the Clapeyron equation we obtain the following equation:

$$\frac{d \ln P}{dT} = \frac{\Delta^v H}{RT^2} \qquad \text{(IV.13)}$$

Known as ***Clausius – Clapeyron equation***, it is valid for evaporation and sublimation processes. If we assume that $\Delta^v H$ (heat of vaporization) is constant, we can perform the integration of above equation and get:

$$\ln \frac{P_2}{P_1} = \int_{T_1}^{T_2} \frac{\Delta^v H}{RT^2} \cdot dT = \frac{\Delta^v H}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad \text{(IV.14)}$$

If the natural logarithm of the vapor pressure is plotted versus the reciprocal of the absolute temperature, we will obtain a straight with the slope equal to $(-{}^{\Delta H}/_{R})$. It is observed experimentally that the vapor pressures of most substances agree quite well with an equation of this type. This assumption will be demonstrated by an experimental work in which it will be determine the heat of vaporization for water.

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- ***Binary systems***

Let's consider the equilibrium:

$$(C_1 + C_2)^l \Leftrightarrow (C_1 + C_2)^g \qquad \text{(IV.15)}$$

This equilibrium can be treated at constant pressure or constant temperature.

If we consider that T = constant, the total pressure of gas phase can be additive calculated by using of Raoult's and Henry's Laws. Under the consideration that the vaporization of solvent and dissolved component are independent we can obtain the equations for vapor and liquid curves, by using of Nernst distribution law and the variation of Nernst constant in respect with pressure, in the following forms:

$$P = P_1^0 + x_2^l \cdot \left(P_2^0 - P_1^0\right) \qquad \text{the liquid curve} \qquad \text{(IV.16)}$$

$$\frac{1}{P} = \frac{1}{P_1^0} + x_2^g \cdot \left(\frac{1}{P_2^0} - \frac{1}{P_1^0}\right) \qquad \text{the vapor curve} \qquad \text{(IV.17)}$$

These equations are valid under the assumption that both phases are ideal. One observes that the liquid curve represents a straight line and the vapor curve is a hyperbola. In the case of non-ideal solutions the equilibrium equations must be corrected by introduction of activity coefficients, and the equilibrium curves will have hyperbolic shapes.

If we consider that P = constant, a similar treat leads to following phase equilibrium equations (van Laar equations):

$$x_2^l = \frac{e^{\lambda_1} - 1}{e^{\lambda_1} - e^{-\lambda_2}} \qquad \text{the liquid curve} \qquad \text{(IV.18)}$$

$$x_2^g = \frac{e^{\lambda_1} - 1}{e^{\lambda_1 + \lambda_2} - 1} \qquad \text{the vapor curve} \qquad \text{(IV.19)}$$

where: $\lambda_1 = \ln K_1 = \frac{\Delta^v H_1^0}{R} \cdot \left(\frac{1}{T_1^0} - \frac{1}{T}\right)$, and $-\lambda_2 = \ln K_2 = \frac{\Delta^v H_2^0}{R} \cdot \left(\frac{1}{T_2^0} - \frac{1}{T}\right)$

When the vapor pressures of pure components have a small difference between their values it is possible the appearance on the total pressure curve of a minimum or a maximum even in the case of little deviations from an ideal behavior. A similar behavior is observed for binary liquid systems with greater deviations from ideality where one observes an extreme point on the curve pressure – composition. A minimum is typical of substances capable of dissociation, a maximum of substances capable of association. The presence of extrema (minimum or maximum) indicates that the composition of the phases is identical (figure IV.1)

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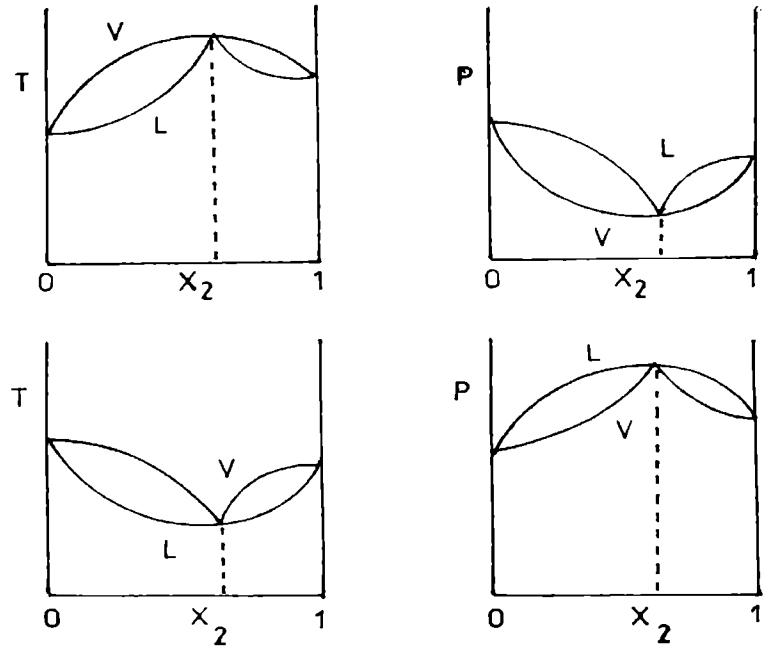

Figure IV.1

Mixture for which the vapor in equilibrium with the liquid has the same composition in the given conditions as the liquid mixture are called ***azeotropic***. These mixtures are also called constant boiling, because upon distillation a condensate is formed having the same composition as the original mixture, and in this conditions separation of a mixture is impossible.

Table IV.1 Boiling temperatures and composition of azeotropic mixture with minimum

C_1^l	C_2^l	t_1^0 (^{0}C)	t_2^0 (^{0}C)	t_{az} (^{0}C)	% C_2^l
H_2O	C_2H_5OH	100	78.30	78.15	95.57
H_2O	n-C_3H_7OH	100	97.19	87.72	78.69
$(CH_3)_2CO$	CS_2	56.25	46.25	39.25	67
$CHCl_3$	C_2H_5OH	61.2	78.2	59.3	6.8

Table IV.2 Boiling temperatures and composition of azeotropic mixture with maximum

C_1^l	C_2^l	t_1^0 (^{0}C)	t_2^0 (^{0}C)	t_{az} (^{0}C)	% C_2^l
H_2O	HCl	100	-85	110	20.3
H_2O	HI	100	-34	127	57
H_2O	HNO_3	100	86	120.5	68

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The azeotropic mixture can be positive (with a minimum on T – x curve) or negative (with a maximum on T – x curve) upon the deviation from the Raoult's law.

From the azeotropic mixtures it is not possible to separate the components from simple or fractionated distillation. In the case of an azeotrope with minimum distillation at any composition gives in the vapor phase the azeotropic mixture, and the liquid phase will be concentrated in one of components, depending from which part of minimum is situated the system that distills. Consequently by a distillation of a binary system having an azeotrope with maximum, in the vapor phase, only one pure component will pass, while in the liquid phase will remain a solution having azeotropic composition. The azeotropic mixture is not a definite compound because as in the case of eutectic, its composition is modified with the working pressure. For example, the mixture water ($t_1^0 = 100^0 C$)– etilic alcohol ($t_2^0 = 78.3^0 C$) forms at 1 atm an azeotrope with $t_{az} = 78.12^0 C$ and 95.57 % alcohol. At pressure P = 100 mm Hg, $t_{az} = 34.2^0 C$ and concentration in alcohol 99.6 moles. Any attempt to obtain a pure alcohol is not efficient. One possibility of obtaining pure alcohol consists in the adding of a third component. In the case of water – etilic alcohol system, when benzene is added a system with two layers is obtained: one is aqueous phase and the other is benzenic phase. Further, it is possible to obtain pure alcohol from benzenic phase.

As an application of azeotropic mixtures we will study in the laboratory the system water – n-propanol, by using of an original device.

IV. c. SOLUBILITY OF GASES IN LIQUIDS

Numerous examples in nature illustrate the ability of liquids to dissolve gases; indeed, human life would not be possible if blood could not dissolve oxygen, nor could marine life exist if oxygen did not dissolve in water. Gas mixtures can be separated by absorption because different gases dissolve in a liquid in different amounts and therefore, most gaseous mixtures can be separated by contact with suitable solvent that dissolves one gaseous component more than another. In the industry of ammonia a very important technological procedure (named Purisol), that uses as selective solvent poly – ethylene - glycols, allows a very good separation of hydrogen and nitrogen from mixture of $H_2 + CO_2 + N_2$.

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The solubility of a gas in liquid is determined by the equations of phase equilibrium. If the gaseous phase and a liquid phase are in equilibrium, then for any component I the fugacities in both phases must be the same:

$$f_i^g = f_i^l \qquad \text{(IV.20)}$$

The simplest way to reduce equation (IV.20) to a useful form is to rewrite it in a manner suggested by Raoult's law. In doing so, we introduce several drastic but convenient assumptions. Neglecting all gas-phase nonidealities as well as the effect of pressure on the condensed phase and also neglecting any nonidealities due to solute-solvent interactions, the equation of equilibrium can be much simplified by writing

$$P_i = x_i^l \cdot P_i^s \qquad \text{(IV.21)}$$

where P_i is the partial pressure of component i in the gas phase, x_i is the solubility (mole fraction) of i in the liquid, and P_i^s is the saturation pressure of pure liquid i at the temperature of the solution. The solubility x_i is called the *ideal solubility* of the gas. In some cases, where the physical properties of solute and solvent are similar, the ideal solubility is remarkably close to the experimental value, but this ideal solubility suffers from two serious defects. First, it is independent of the nature of the solvent, i.e., a given gas at a fixed temperature and partial pressure, has the same solubility in all solvents and second, the solubility of gas always decreases with rising temperature. This last prediction is frequently correct but not always: for example, near room temperature, the solubility of light gases (H_2, He, Ne) increase with rising temperature in most solvents.

It was observed that the solubility of a gas in a liquid is often proportional to its partial pressure in the gas phase, provided that the partial pressure is not large. The equation that describes this observation is known as ***Henry's Law***:

$$P_i = x_i^g \cdot P = k \cdot x_i^l \qquad \text{(IV.22)}$$

where, for any given solute and solvent, k is a constant of proportionality depending only of temperature. The above equation provides an excellent approximation when the solubility and the partial pressure of the solute are small and when the temperature is well below the critical of the solvent.

The assumptions leading to equation (IV. 22) can readily be recognized by comparing it with equation (IV.20). A comparison of the left-hand size shows that in Henry's law the gas phase is assumed to be ideal and thus the fugacity is replaced by the partial pressure. A comparison of the right-hand size shows that the fugacity in the liquid phase is assumed to be proportional to the mole fraction

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and that the constant of proportionality is taken as an empirical factor that depends on the natures of solute and solvent and on the temperature. The thermodynamic significance of this constant can be establish by comparing the liquid fugacity as given by Henry's law with that obtain in the more conventional manner using the concept of an activity coefficient γ and standard state fugacity f^0:

$$f_2^l = k \cdot x_2^l = H_{2,1} \cdot x_2^l = \gamma_2^l \cdot x_2^l \cdot f_2^{0,l} \tag{IV.23}$$

Thus,

$$k = H_{2,1} = \gamma_2^l \cdot f_2^{0,l} \tag{IV.24}$$

As indicated by equation (IV.22) Henry;s law assume that the gas-phase fugacity is equal to the partial pressure. This assumption will be removed by including the gas-phase fugacity coefficients γ_2^l:

$$f_2^l = \gamma_2^g \cdot x_2^g \cdot P = H_{2,1} \cdot x_2^l \tag{IV.25}$$

At high pressures it is necessary to consider how Henry's constants depend on pressure. This dependence can be obtained by using the equation:

$$\left(\frac{\partial f_2^l}{\partial P}\right)_{T,x_2^l} = \frac{\overline{V}_2}{R \cdot T} \tag{IV.25}$$

When we consider the partial molar volume of solute at infinite dilution $\overline{V}_2^{\infty,l}$, finally we obtain the equation:

$$\ln \frac{f_2^g}{x_2^l} = \ln H_{2,1}^{P_1^s} + \frac{\overline{V}_2^{\infty,l} \cdot \left(P - P_1^s\right)}{R \cdot T} \tag{IV.26}$$

where P_1^s represents the saturation pressure of the solvent. This equation is very useful for representing solubilities of sparingly soluble gases up to high pressure.

An originally equipment existing in our laboratory allows to determine solubility of gases in liquids at different pressures and temperatures.

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- ***Systems with eutectic***

The easiest binary liquid – solid equilibrium is the system in which the pure components crystallized from solution and melt respectively where they are complete miscible.

For a binary system with miscible components in the liquid phase and non-miscible in the solid phase, the phase equilibria can be written:

$$\begin{aligned} (C_1 + C_2)^l &\Leftrightarrow C_1^s \\ (C_1 + C_2)^l &\Leftrightarrow C_2^s \end{aligned} \qquad \text{(IV.27)}$$

By using of Nernst distribution law and the thermodynamic equation of an isobaric equilibrium, we obtain:

$$K_1 = \frac{x_1^s}{x_1^l} = \frac{1}{x_1^l} \qquad K_2 = \frac{x_2^s}{x_2^l} = \frac{1}{x_2^l} \qquad \text{(IV.28)}$$

$$\ln K_1 = \int_{T_1^0}^{T} \frac{\Delta^s H_1^0}{RT^2} dT = -\frac{\Delta^s H_1^0}{R}\left[\frac{1}{T} - \frac{1}{T_1^0}\right] \qquad \text{(IV.29)}$$

or $$\ln x_1^l = \frac{\Delta^s H_1^0}{R}\left[\frac{1}{T} - \frac{1}{T_1^0}\right] \qquad -\ln\left(1 - x_2^l\right) = \frac{\Delta^l H_1^0}{R}\left[\frac{1}{T} - \frac{1}{T_1^0}\right] \qquad \text{(IV.30)}$$

and similarly: $$\ln K_2 = \int_{T_2^0}^{T} \frac{\Delta^s H_2^0}{RT^2} dT = -\frac{\Delta^s H_2^0}{R}\left[\frac{1}{T} - \frac{1}{T_2^0}\right] \qquad \text{(IV.31)}$$

or $$-\ln x_2^l = \frac{\Delta^m H_2^0}{R}\left[\frac{1}{T} - \frac{1}{T_2^0}\right] \qquad \text{(IV.32)}$$

In the equations (IV.30) and (IV.32), $\Delta^m H_1^0 = \overline{H}_1^l - H_1^s$ and $\Delta^m H_2^0 = \overline{H}_2^l - H_2^s$ represent the heats of melting of the pure components at their normal melting points. The (IV.30) and (IV.32) are the cooling curve equations (or liquidus curves).

The eutectic composition and eutectic temperature are given by the intersection of the two liquidus curves and can be estimated by solving simultaneously of these two equations, on the assumption that the liquid represents an ideal solution with respect to both components over its entire composition range.

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Liquid – solid equilibrium diagrams are construct by using of cooling curves (method of thermal analysis). Mixtures having different composition will be heated at higher temperature in comparison with melting temperatures of pure components. At cooling, temperature variation in time is recorded. In the following diagram is presented the method that allows obtaining the eutectic temperature and composition by using of cooling curves of pure components and mixtures.

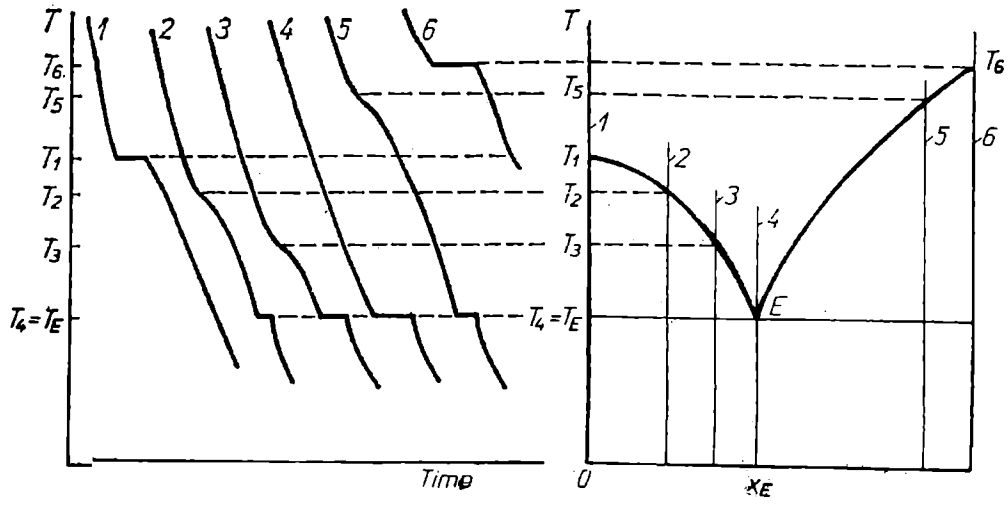

Figure IV.2 Cooling curves for a system with one eutectic

In this figure T_1-E and E-T_6 represent crystallization curves.

- *Composition 1.* The component C_1 (pure) crystallized at temperature T_1. At this temperature heat of crystallization is emitted, temperature remains constant and on the cooling curve a landing is recorded.
- *Composition 2.* The melt contains two components. By cooling at T_2, the liquid is saturated in C_1 component, and from the melt the first crystals of C_1 will fall. Because the heat of crystallization is emitted, we can observe an inflection point on the cooling curve. In comparison with composition 1, the temperature doesn't remain constant. When the temperature of the system attains the value T_E and the composition of the liquid phase attains value x_E (***the eutectic point***), the simultaneous crystallization of the two components will be made. Here, the crystallization will be done without changing the composition and on the cooling curve 2, at T_E, a landing will appear.
- *Composition 3.* The cooling curve has the same shape as in the case of composition 2 but the falling of the first crystals will take place at a lower temperature.
- *Composition 4.* Corresponds to eutectic point. At this temperature the liquid having the eutectic composition will crystallize.

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- *Composition 5*. At T_5 the first crystals from C_2 will appear and the cooling curve is similar with those of 2 and 3 compositions.
- *Composition 6*. Corresponds to pure C_2.

In the region above the crystallization curves (the melt region), the system has two degrees of freedom – the temperature and composition can be changed arbitrarily and the number of phases (one phase) will remain constant. At point E where three phases are in equilibrium, i.e., the liquid eutectic and the solids components C_1^s and C_2^s, the system is conditionally invariant.

As solid –liquid equilibrium with eutectic we will study in laboratory p-nitro-phenol – naphthalene.

- ***Temperature dependence of solubility***

When a solid is brought into contact with a liquid in which it can dissolve, a certain amount of it passes into solution, until the solution is saturated. In all determinations of the solubility it is necessary, no only to determine the amount of dissolved substance in the solution, but also to ascertain the nature of the solid phase which is in equilibrium with the solution.

The amount of substance dissolved depends, also, on the temperature; the *solubility* of a substance, or the number of grams of substance dissolved by a given weight of the solvent, may either increase or decrease with rise of temperature, according to whether the dissolution is endothermic or exothermic, respectively. In all cases, however, the solubility curve of any substance is continuous so long as the solid substance in contact with the solution remains unchanged. If, however, a change in the solid phase occurs, the solubility curve will show a "break" or discontinuous change in direction.

It takes an appreciable time to saturate a liquid with the solid. The length of time required not only varies with the state of subdivision of the solid and the efficiency of the shaking or stirring, but is also dependent on the nature of the substance. In all cases, therefore, care must be taken that sufficient time is allowed for equilibrium to be established more especially when changes in the solid may occur.

In cases where the solubility increases with rise if temperature, the time required for the attainment of equilibrium can generally be shortened by preparing a saturated solution at a higher temperature and allowing it to cool to the desired temperature in contact with the solid phase. Particular care, however, must be exercised in cases where the solid phase itself undergoes change with the temperature.

If we dissolve one mole of a substance in such an amount of pure solvent that will give us a solution of the given composition, than the heat effect observed is called *the integral heat of solution (dissolution)*.

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The integral heat of dissolution for a solid in a saturated solution can be exactly determined by measuring its solubility at different temperatures.

The relation between molar fraction of the solid and temperature is:

$$\left(\frac{\partial \ln x_2}{\partial T}\right)_{P,x_1} = \frac{\Delta H_{dis}^{sat}}{R \cdot T^2} \qquad \text{(IV.33)}$$

which is so-called Schroder's logarithmic curve (1890). Integrating equation (IV. 33), we get:

$$\ln x_2^{sat}(T) = -\frac{\Delta H_{dis}^{sat}}{R \cdot T} + const. \qquad \text{(IV.34)}$$

or $$\lg x_2^{sat}(T) = -\frac{\Delta H_{dis}^{sat}}{2.303 \cdot R \cdot T} + const. \qquad \text{(IV.35)}$$

where x_2^{sat} is the solubility of the solid.

The solubility in an ideal solution will be limited only when $T<T_f$ (T_f represents the temperature of fusion), i. e. when the pure component is in a different state of aggregation. Since $\Delta^f H > 0$ (enthalpy of fusion), the solubility always grows with increasing temperature.

If we integrate the equation (IV. 33):

$$\int_{x_2^{sat}}^{1} d\ln x_2 = \int_{T}^{T_f} \frac{\Delta^f H}{R \cdot T^2} dT \qquad \text{(IV.36)}$$

we get: $$\ln x_2^{sat} = -\frac{\Delta^f H}{R} \cdot \left(\frac{1}{T_f} - \frac{1}{T}\right) \qquad \text{(IV.37)}$$

It is easy to verify equations (IV.35) or (IV.37) graphically; if a solution is ideal, the relationship $\lg x_2 = f\left(1/T\right)$ is linear; when continued to the region of high temperatures, the straight line will reach the point with the coordinates $\lg x_2 = 0$ and $1/T = 1/T_f$ and will have a slope corresponding to the value of $\Delta^f H$.

As application of this chapter we will study variation of solubility with temperature for two systems namely: $KNO_3 + H_2O$, and naphthalene + benzene and from experimental data, the integral heat of dissolution for a solid in a saturated solution can be exactly determined.

- ***Determination of activity coefficients from cryoscopic measurements***

The cryoscopic method has large applications in the thermodynamics. For example, this method is used for determination of melting heats of metals and molten salts. These substances are melted at very high temperatures and the direct determinations of enthalpy of mixing are very difficult. In the

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following table we present the cryoscopic constants of some substances having very high values fact that favors the precision of experimental measurements:

Table IV.3 Some values of cryoscopic constants

Solvent	$t_0^m\ [^0C]$	k_c
Water	0	1.86
Benzene	5.5	5.08
Camphor	179.5	40
Lead (liquid)	327	125
Iron (liquid)	1536	101.5
Tin (liquid)	232	35.35
$BaCl_2$ (liquid)	962	108

Investigations at high temperatures are favored, due to these very high cryoscopic constants. In the case of organic systems, camphor is priority used.

In this chapter we will present a particular case of application of liquid – solid equilibrium, namely: equilibrium electrolyte solution – pure solvent:

$$(C_1 + C_2)^l \Leftrightarrow C_1^s \qquad \text{(IV.38)}$$

If we note by $\Delta^s H_{T_1}$ - the solidification heat of solvent at freezing point of solution, and by $\Delta^s H_{T_1^0}$ - the solidification heat of solvent at freezing point of pure solvent, according Kirrchoff's Law, between these two thermal effects, the following relation can be written:

$$\Delta^s H_{T_1} = \Delta^s H_{T_1^0} - \Delta C_P \cdot \theta \qquad \text{(IV.39)}$$

where: $\Delta C_P = C^s_{P_1\,solid} - \overline{C}_{P_1\,liquid}$

and $\theta = T_1^0 - T_1 = -\Delta T$

In solid phase of considered equilibrium there are only solvent crystals, and the molar fraction of solvent is $x_1^s = 1$ and activity coefficient is $\gamma_1^s = 1$; therefore $x_1^s \cdot \gamma_1^s = 1$ or the solvent activity in solid phase, $a_1^s = 1$. In liquid phase represented by the solution formed from components C_1 and C_2; $x_1^l \cdot \gamma_1^l \neq 1$ or $x_1^l \cdot \gamma_1^l = a_1^l$ (thermodynamic activity of C_1 in liquid phase).

For component C_1, distributed between liquid and solid phase, the Nernst distribution constant is: $K = \dfrac{a_1^s}{a_1^l} = \dfrac{1}{a_1^l} \Rightarrow \ln K = -\ln a_1^l$ (IV.40)

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The temperature variation of Nernst distribution constant is:

$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta^s H_{T_1}}{RT_1^2}$ and derivating the eq. (IV. 40) we obtain :

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = -\left(\frac{\partial \ln a_1^l}{\partial T}\right)_P \qquad \text{(IV.41)}$$

So,

$$\left(\frac{\partial \ln a_1^l}{\partial T}\right)_P \cdot dT = -\frac{\Delta^s H_{T_1}}{RT_1^2} \cdot \mathrm{dT} \Rightarrow \mathrm{d}\ln a_1^l = \frac{\Delta^s H_{T_1^0} - \Delta C_P \cdot \theta}{R\left(T_1^0\right)^2 \cdot \left(1 - \theta / T_1^0\right)^2} \cdot d\theta \quad \text{with} \quad \left(dT = -d\theta\right) \qquad \text{(IV.42)}$$

After the calculations we obtain:

$$d\ln a_1 = \frac{1}{R \cdot \left(T_1^0\right)^2} \cdot \left[\Delta^s H_{T_1^0} + \left(\frac{2 \cdot \Delta^s H_{T_1^0}}{T_1^0} - \Delta C_P\right) \cdot \theta + \left(\frac{3 \cdot \Delta^s H_{T_1^0}}{\left(T_1^0\right)^2} - \frac{2 \cdot \Delta C_P}{T_1^0}\right) \cdot \theta^2 + \ldots\right] \cdot d\theta \qquad \text{(IV.43)}$$

Integrating the above equation we will obtain the activity of solid solvent at the freezing temperature of the solution:

$$\log a_1 = \frac{1}{2.303 \cdot R \cdot \left(T_1^0\right)^2} \cdot \left[\Delta^s H_{T_1^0} \cdot \theta + \left(\frac{\Delta^s H_{T_1^0}}{T_1^0} - \frac{\Delta C_P}{2}\right) \cdot \theta^2 + \left(\frac{\Delta^s H_{T_1^0}}{\left(T_1^0\right)^2} - \frac{2 \cdot \Delta C_P}{3 \cdot T_1^0}\right) \cdot \theta^3 + \ldots\right] \qquad \text{(IV.44)}$$

$\Delta^s H_{T_1^0}$, T_1^0 and ΔC_P are specified quantities for pure solvent and are constant for aqueous solutions.

For the evaluation of thermodynamic activity of water contained in aqueous solutions, we can use the following relation deduced from equation (IV.44):

$$\log a_1 = -0.004211 \cdot \theta - 0.0000022 \cdot \theta^2 \qquad \text{(IV.45)}$$

In the calculation of activity of dissolved component the Gibbs – Duhem equation is applied:

$$x_1 \cdot d\ln a_1 + x_2 \cdot d\ln a_2 = 0 \qquad \text{(IV.46)}$$

For aqueous solutions: $x_1 = \frac{55.51}{m + 55.51}$ and $x_2 = \frac{m}{m + 55.51}$ so that:

$$d\ln a_2 = \frac{55.51}{R \cdot m \cdot \left(T_1^0\right)^2} \cdot \left[\Delta^s H_{T_1^0} + \left(\frac{2 \cdot \Delta^s H_{T_1^0}}{T_1^0} - \frac{\Delta C_P}{2}\right) \cdot \theta.\right] \cdot d\theta \qquad \text{(IV.47)}$$

In very dilute solutions, when $\theta \to 0$ and $a_2 \to m$ equation (IV.47) will become:

$$\frac{dm}{m} = \frac{55.51}{R \cdot m \cdot \left(T_1^0\right)^2} \cdot \Delta^s H_{T_1^0} \cdot d\theta \qquad \text{(IV.48)}$$

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We define as cryoscopic constant: $k_c = \frac{R \cdot (T_1^0)^2}{55.51 \cdot \Delta^s H_{T_1^0}}$ (IV.49)

For an ideal solution: $\theta = k_c \cdot m$ (IV.50)

When the solution has a non-ideal behavior, the equation (IV.50) must be corrected by introduction of a deviation factor defined by the relation:

$$j = 1 - \frac{\theta}{k_c \cdot m} \qquad \Rightarrow \qquad \frac{\theta}{k_c} = m \cdot (1 - j) \tag{IV.51}$$

After derivating:

$$\frac{d\theta}{k_c} = dm - mdj - jdm \quad \text{or} \quad \frac{d\theta}{k_c \cdot m} = (1 - j) \cdot d \ln m - dj \tag{IV.52}$$

From equations (IV.47), (IV.48) and (IV.52) one obtain:

$$d \ln \frac{a_2}{m} = -jd \ln m - dj + \frac{55.51}{R \cdot (T_1^0)^2} \cdot \left(\frac{2 \cdot \Delta^s H_{T_1^0}}{T_1^0} - \Delta C_P \right) \cdot \frac{\theta}{m} \cdot d\theta \tag{IV.53}$$

By integration of this equation from m = 0 to a value m, the following expression is established:

$$\ln \frac{a_2}{m} = -\int_0^m \frac{j}{m} dm - (j - j_0) + \frac{55.51}{R \cdot (T_1^0)^2} \cdot \int_{\theta(0)}^{\theta(m)} \left(\frac{2 \cdot \Delta^s H_{T_1^0}}{T_1^0} - \Delta C_P \right) \cdot \frac{\theta}{m} \cdot d\theta \tag{IV.54}$$

The general equation of activity coefficient is:

$$\ln \gamma_2 = \ln \gamma_0 - \int_0^m \frac{j}{m} dm - (j - j_0) + \frac{55.51}{R \cdot (T_1^0)^2} \cdot \int_{\theta(0)}^{\theta(m)} \left(\frac{2 \cdot \Delta^s H_{T_1^0}}{T_1^0} - \Delta C_P \right) \cdot \frac{\theta}{m} \cdot d\theta \tag{IV.55}$$

where γ_0 is the activity coefficient of the dissolved component at infinite dilution. The two integrals can be solved by graphical method. The obtained values for γ_2 represent the values of activity coefficients of dissolved component at the freezing point of the solution.

Other applications of phase equilibria will be discuss in the experimental part of this book:

- Determination of activity coefficients of the solute from cryoscopic measurements;
- Determination of molecular weights by using of following methods: elevation of the boiling point, depression of freezing point and from osmotic pressure measurements.

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Composition triangle

The composition of a system is depicted by points of an equilateral triangle. Its apices correspond to the individual substances, the points on its sides to the relevant two-component systems, and the points inside the triangle to ternary mixtures (figure IV.3). Since the composition is generally expressed as a fraction or per cent (mole fraction, or weight or mass per cent), the sides of the triangle are divided into 100 (or 10) parts, and straight lines parallel to the respective sides are drawn through the points of division.

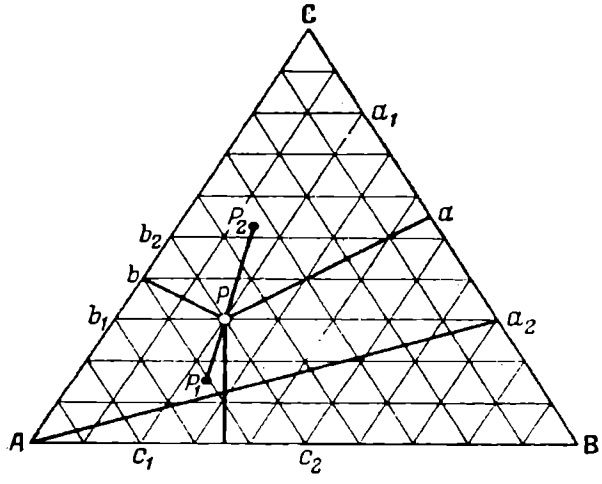

Figure IV.3 Depicting the composition of three-component systems (composition triangle)

The ratios of the components are determined either on the basis of the fact that the sum of perpendiculars dropped from any point onto the sides of an equilateral triangle equals its altitude, taken equal to 1 or 100 (*Gibbs's method*), or that the sum of lines drawn from any point inside an equilateral triangle parallel to its sides up to their intersection with another side of the triangle equals a side of the triangle, which is taken equal to 1 or 100 (*Roozeboom's method*).

Thus, by the former method, the content of components A, B and C in the system which point P corresponds to is expressed by lengths Pa, Pb and Pc, respectively. According to the latter method, it is

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expressed by lengths $Pa_1 = Bc_2$, $Pb_1 = Ac_1$ and $Pc_2 = c_1c_2$ (or $Pc_1 = c_1c_2$, $Pa_2 = Bc_2$ and $Pb_2 = Ac_1$). Therefore, system P contains 50% of substance A, 20% of B and 30% of C.

Both methods give the same result, since the sides and altitudes of an equilateral triangle are proportional to one another.

It is obvious that:

- With a reduction in the concentration of a given component, the point characterizing the composition of the mixture shifts in a direction opposite to the apex corresponding to it (thus, shifting along Aa_2 toward a_2 indicates lowering of the content of A);
- A straight line parallel to a side opposite to a given apex is a line of constant content of the component which this apex corresponds to (for example any point on line b_2Pc_2 corresponds to 50% of A);
- A straight line passing through the apex of the triangle corresponding to a given component is a line corresponding to a constant ratio between the two other components (for example at any point on line Aa_2 the ratio between B and C is 7 : 3);
- If a given system is obtained from two others (decomposes into two others) then, as was the case for one- and two-component mixtures, the figurative points of all the systems are on one straight line (the *rule of straight tie lines*) and are arranged so that the ratio between the amounts of the two constituent systems is determined by the lever rule. For instance, if system P can be decomposed into systems P_1 and P_2 or obtained from them, point P must be on straight line P_1P_2, and:

$$\frac{amount\ of\ P_1}{amount\ of\ P_2} = \frac{PP_2}{PP_1}$$

- If a system is composed of three others, its figurative point should be at the center of gravity (*center of gravity rule*, a particular case of which is the lever rule).

The system benzene – methanol – water will be study as an example as ternary equilibrium.

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V. EXPERIMENTAL APPLICATIONS

V. 1. PARTIAL MOLAR VOLUMES

In this experiment, the partial molar volumes of methanol and water will be calculated as a function of molar fractions. The densities will be measured with a pycnometer.

METHOD

In this experiment, the partial molar volumes of methanol and water will be calculated by using the ***method of intersection*** applied to binary systems with miscible components in any proportion. This method analyzes the dependence of the average molar volume of a mixture upon composition. To illustrate this procedure, let us consider a two – component system with mole numbers n_1 (H_2O – solvent) and n_2 (CH_3OH – solute) and mole fractions x_1 and x_2. The average molar volume, V, can be written in the form:

$$V = \frac{\mathbf{V}}{n_1 + n_2} = \frac{n_1\overline{V_1} + n_2\overline{V_2}}{n_1 + n_2} = x_1\overline{V_1} + x_2\overline{V_2} \qquad \text{(V.1-1)}$$

The average molar volume is plotted versus molar fraction of dissolved component (x_2). The tangent on curve in a point intersects the volume axes in points B (at $x_2 = 0$) and B' (at $x_2 = 1$).

The correspondence between physical and geometrical quantities is demonstrated by means of thermodynamics. From figure V.1-1:

$$\overline{V_1} = AB; \overline{V_2} = A'B'; AC = A'C' = V \qquad \text{(V.1-2)}$$

Differentiating V from equation (V.1-1) partially with respect to x_2 and considering a special form of Gibbs – Duhem equation, we obtain the result:

$$\left(\frac{\partial V}{\partial x_2}\right)_{T,P,x_1} = \overline{V_2} - \overline{V_1} \qquad \text{(V.1-3)}$$

Using equations (V.1-1) and (V.1-3), the expressions for $\overline{V_1}$ and $\overline{V_2}$ can be obtained:

$$\overline{V_1} = V - x_2\left(\frac{\partial V}{\partial x_2}\right)_{T,P,x_1} \qquad \text{(V.1-4)}$$

$$\overline{V_2} = V + x_1\left(\frac{\partial V}{\partial x_2}\right)_{T,P,x2} \qquad \text{(V.1-5)}$$

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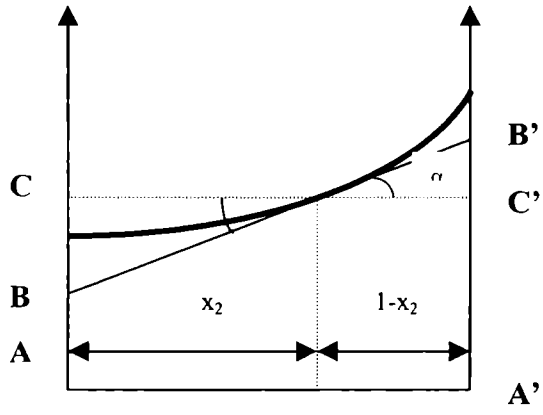

Figure V.1-1 Dependence of average molar volume upon molar fraction of dissolved component

From figure V.1-1 we can observe that:

$$\overline{V_1} = AB = V - BC = V - x_2\left(\frac{\partial V}{\partial x_2}\right)_{T,P,x_1} \qquad \overline{V_2} = A'B' = V + B'C' = V + x_1\left(\frac{\partial V}{\partial x_2}\right)_{T,P,x2}$$

$$tg\alpha = \frac{BC}{x_2} \Rightarrow BC = x_2 tg\alpha = x_2\left(\frac{\partial V}{\partial x_2}\right)_{x1} \qquad tg\alpha = \frac{B'C'}{1-x_2} = \frac{B'C'}{x_1} \Rightarrow B'C' = x_1 tg\alpha = x_1\left(\frac{\partial V}{\partial x_2}\right)_{x2}$$

APPARATUS AND CHEMICALS

- Pycnometers used for density determination, volumetric flasks, pipettes, syringe, wind instrument, analytical balance, filter paper:
- Distilled water, pure methanol.

EXPERIMENTAL

Using the volumetric flasks and indications from table V.1-1, make up 5 solutions methanol – water. The resulted concentrations are those from table V.1-1.

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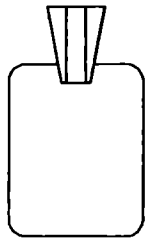

Figure V.1-2 Pycnometer

The pycnometer is rinsed with distilled water and thoroughly dried before each use. Use a wind instrument and rinse and dry by suction. The filling of a pycnometer must be carried out with great care. Fill the pycnometer body with liquid and seat the capillary stopper firmly. Wipe off excess liquid around the tapered joint, including the cap, but not including the tip of the stopper. Cap the pycnometer, place it in the balance and weight it using an analytical balance.

CALCULATIONS

- *Determination the pycnometer volume*

  -the pycnometer should be weighted empty and dry (m_p) and also with distilled water in it (m_{p+H2O})

  -the pycnometer volume can be calculated with the relation:

$$V_p = \frac{m_{p+H2O} - m_p}{\rho_{H2O}} \qquad \text{(V.1-6)}$$

  Take the value for the water density from the table V.1-1.

- *Determination the density of each solution*

  -fill the pycnometer body with the first solution and weigh it. You will obtain m_{p+sol};

  -repeat the operation for the other solutions.

  The density of each solution can be calculated with the relation:

$$\rho_{sol} = \frac{m_{p+sol} - m_p}{V_p} \qquad \text{(V.1-7)}$$

- *Calculate the average molecular weight $\overline{M}$ of each solution using the relation:*

$$\overline{M} = x_1 M_1 + x_2 M_2 \qquad \text{(V.1-8)}$$

  where M_1 and M_2 are molecular weights for water (18.015) and methanol (32.04)

- *Determination of average molar volume of each solution*

$$V = \frac{\overline{M}}{\rho_{sol}} \qquad \text{(V.1-9)}$$

- *Plot the average molar volume versus molar fraction of dissolved component V $f(x_2)$;*
- *Determination of partial molar volumes by intersection of one tangent with volume axes;*

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➢ *Present in tabular form the quantities:* m_{p+sol}, m_{sol}, ρ_{sol}, V, $\overline{V_1}$, $\overline{V_2}$ *for each studied solution;*

➢ ✎ *Fill the table with your data.*

Table V.1-1 Experimental data

x_2	V_1 (ml)	V_2 (ml)	m_{p+sol} (g)	m_{sol} (g)	ρ_{sol} (g/ml)	$\overline{M}$ (g/mole)	V (ml/mole)	$\overline{V_1}$ (ml/mole)	$\overline{V_2}$ (ml/mole)
0.0	20.00	0.00			0.998	18.015			
0.2	12.80	7.20							
0.5	6.20	13.80							
0.7	3.20	16.80							
0.8	2.00	18.00							
0.9	0.95	19.05							
1.0	0.00	20.00			0.792	32.04			

CONCLUSIONS AND DISCUSSIONS

➢ examine the shape of the curve and explain the nature of forces between the solution components;

➢ compare the experimental obtained data with those obtained from equations (V.1-4) and (V.1-5);

➢ compare the molar volumes V_1^0 and V_2^0 for pure water and methanol with the obtained values $\overline{V_1}$ and $\overline{V_2}$ from solutions.

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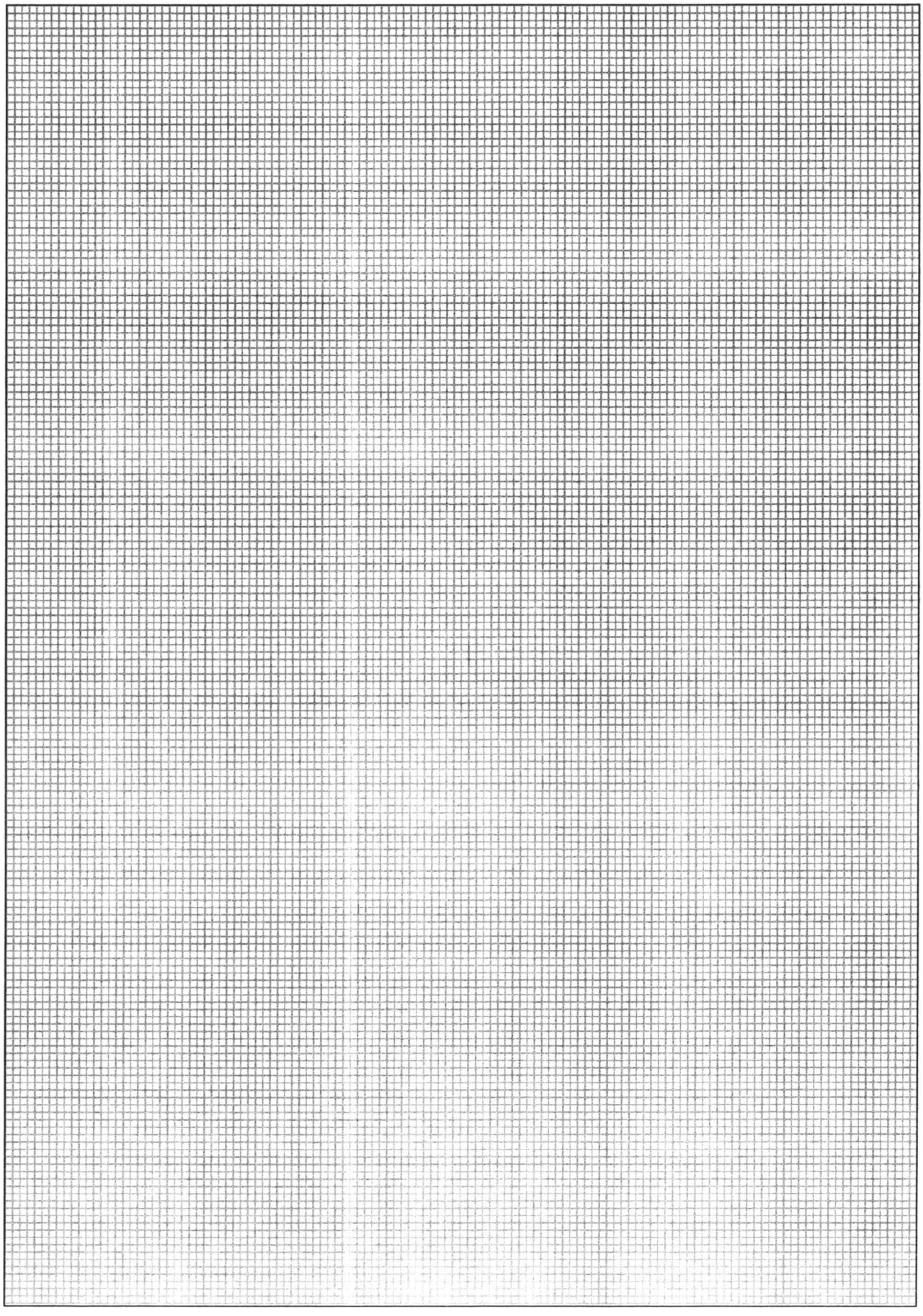

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V.2. DETERMINATION OF THE COMPRESSIBILITY FACTOR BY BURNETT METHOD

The Burnett method allows the determination of the compressibility factor of a real gas from pressure measurements only.

METHOD

The Burnett method represents an experimental procedure, which does not involve direct mass or volume measurements. The principle is based on pressure dropping at the isothermal expansion between calibrated vessels, from a high to minimal detectable pressure. From the practical point of view, the procedure consists in the achievement of a set of successive expansions between two vessels having volumes V_1 and V_2 for a large range of pressures beginning with the maximal one P_0 to minimal value P_i. The mole number of gas before and after each expansion is the same, for example:

$$n = \frac{P_{i-1}}{Z_{i-1}} \cdot \frac{V_1}{R \cdot T} = \frac{P_i \cdot (V_1 + V_2)}{Z_i \cdot R \cdot T} \qquad \text{(V.2-1)}$$

According to the definition of compressibility factor (I.14), one can write:

$$Z_i = \frac{P_i \cdot (V_1 + V_2)}{n_i \cdot R \cdot T} \qquad Z_0 = \frac{P_0 \cdot V_1}{n_i \cdot R \cdot T} \qquad \text{(V.2-2)}$$

By the successive application of (V.2-1) to the i-expansion, it results:

$$P_i \cdot N^i = Z_i \cdot \frac{P_0}{Z_0} \qquad \text{(V.2-3)}$$

where $N = (V_1+V_2) / V_1$ represents the cell constant and ratio P_0 / Z_0 is a constant for a set of measurements, dependent on the initial pressure P_0 as well as the gas compressibility, Z_0. Value $P_0 / Z_0 = A$ is obtained from the graphical plot of the product $P_i \cdot N^i$ versus P_i, the intercept being A. The A value, once known, allows the estimation of the compressibility factor of a real gas from the equation:

$$Z_i = \left(1/A\right) \cdot P_i \cdot N^i \qquad \text{(V.2-4)}$$

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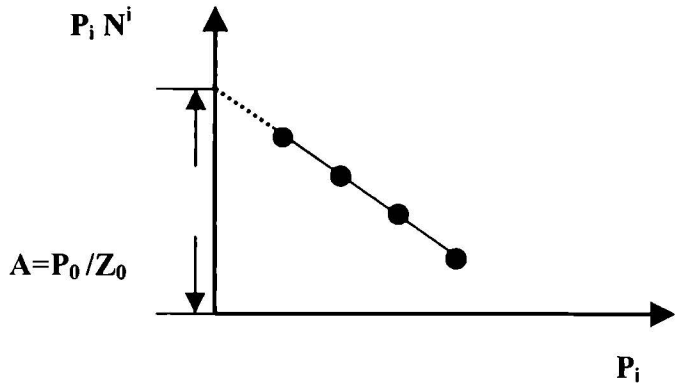

Figure V.2-1
Graphical plot of the product $P_i \cdot N^i$ versus P_i

APPARATUS AND CHEMICALS

- Burnett cell
- Carbon dioxide

The Burnett cell is the main part of the apparatus (figure V.2-2). It is formed from vessels 1 and 2 with the volumes: $V_1 = 115\ cm^3$ and $V_2 = 38\ cm^3$. Vessel 1 is linked with the filling system by means of R_1 valve and with vessel 2 by R_2 valve. The vessel 2 is joint at its turn by R_3 valve to the vacuum system. The Burnett cell, made from stainless steel is perfectly closed by flanges and the teflon gaskets. All connections are made from stainless steel capillary tubes.

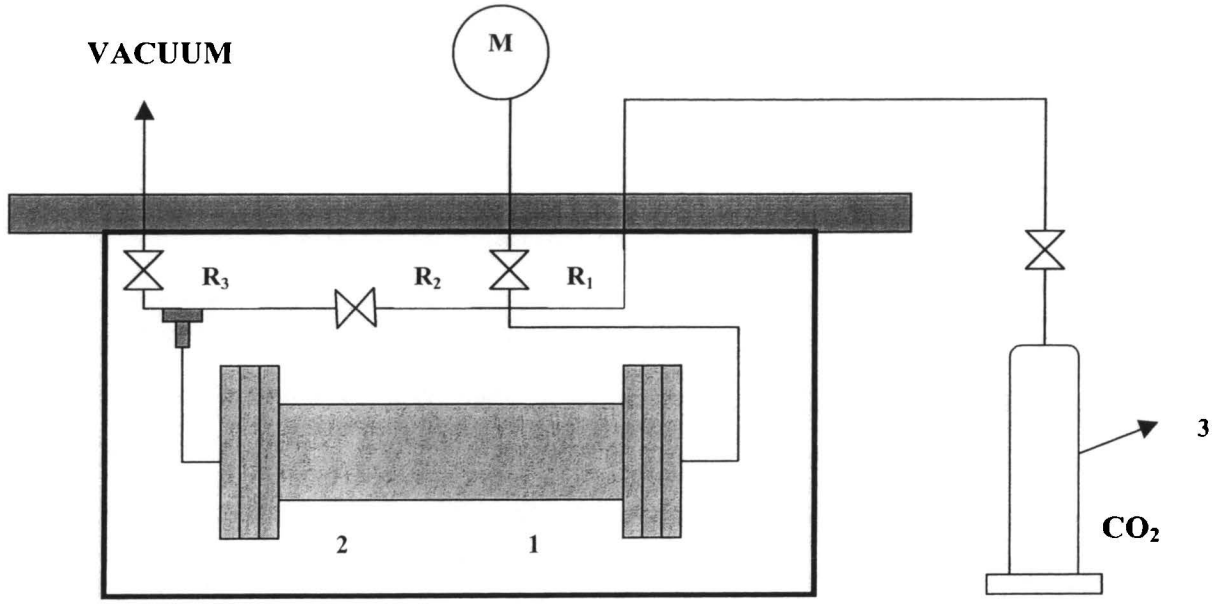

Figure V.2-2 Scheme of the experimental equipment

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The pressure device consists of a Bourdon pressure gauge and the evacuating of the equipment was made with a vacuum pump. The gas filling is made from cylinder (3). In our experiment we work with CO_2.

The determination of N constant is made by means of a gas having a linear isotherm of a compressibility factor. For this purpose helium was used. The value of N constant obtained with helium calibration is equal with 1.306.

EXPERIMENTAL

The both vessels 1 and 2 are, for some minutes, evacuated and after this, vessel 1 is slowly filled with gas from cylinder (3). In the time of this operation we remark that the filling connection is cooled because of the Joule – Thompson effect. After the pressure is stabilized, we note this value equal with P_0. Valve R_2 is then opened and so is obtained the P_1 value. This operation is repeated up to the minimal value approximately equal with 1 bar.

With experimental values P_i we fill the experimental table data (table V.2-2).

CALCULATIONS

- The theoretical values of compressibility factor Z may be calculated using the equations of state and corresponding computing programs. In our case we have used the Beattie – Bridgemann equation of state together with virial equation. These two equations have the form:

$$P = RT\frac{(1-\varepsilon)}{V^2}\cdot(V+B) - \frac{A}{V^2} \qquad \text{(V.2-5)}$$

where:

$$A = A_0\cdot\left(1-\frac{a}{V}\right) \qquad B = B_0\cdot\left(1-\frac{b}{V}\right) \qquad \varepsilon = \frac{c}{V\cdot T^3}$$

in which: a, b, c, A_0, B_0, R are constants.

$$Z_{theor} = \frac{P\cdot V}{R\cdot T} = 1 + \frac{B(T)}{V} \qquad \text{(V.2-6)}$$

At 20^0C, the value of B(T) = -125.7 cm^3/mole.

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➢ Values of molar volumes of CO_2 at 20^0C at different pressures are presented in the following table:

Table V.2-1

P (atm)	V ($cm^3 mole^{-1}$)
0.1	253000
0.2	122320
0.3	82720
0.5	47960
1	24948
2	12188
3	7920
4	5940
5	4796.0
6	3858.8
8	2882.0
10	2332.0
12	1887.6
15	1482.8
20	1078.0
25	814.0
30	560.0
35	536.8
40	433.4
45	363.0
50	308.9

➢ *Present the results in tabular form*:

Table V.2-2 Experimental data

Expansion step		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**...i-1**	**i**
Pressure in the vessels	V_1	P_0 =	P_1 =	P_2 =	P_3 =	P_4 =	P_5 =	P_6 =	P_7 =	P_{i-2}	P_{i-1}
	V_1+V_2	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_{i-1}	P_i
$P_i.N^i$											
Z_{exp}											
Z_{theor}											

CONCLUSIONS AND DISCUSSIONS

➢ Carbon dioxide is a real gas that presents considerable deviations from ideal behavior. This aspect can be easily remarked by comparison of the theoretical and experimental values of compressibility factor at different pressures.

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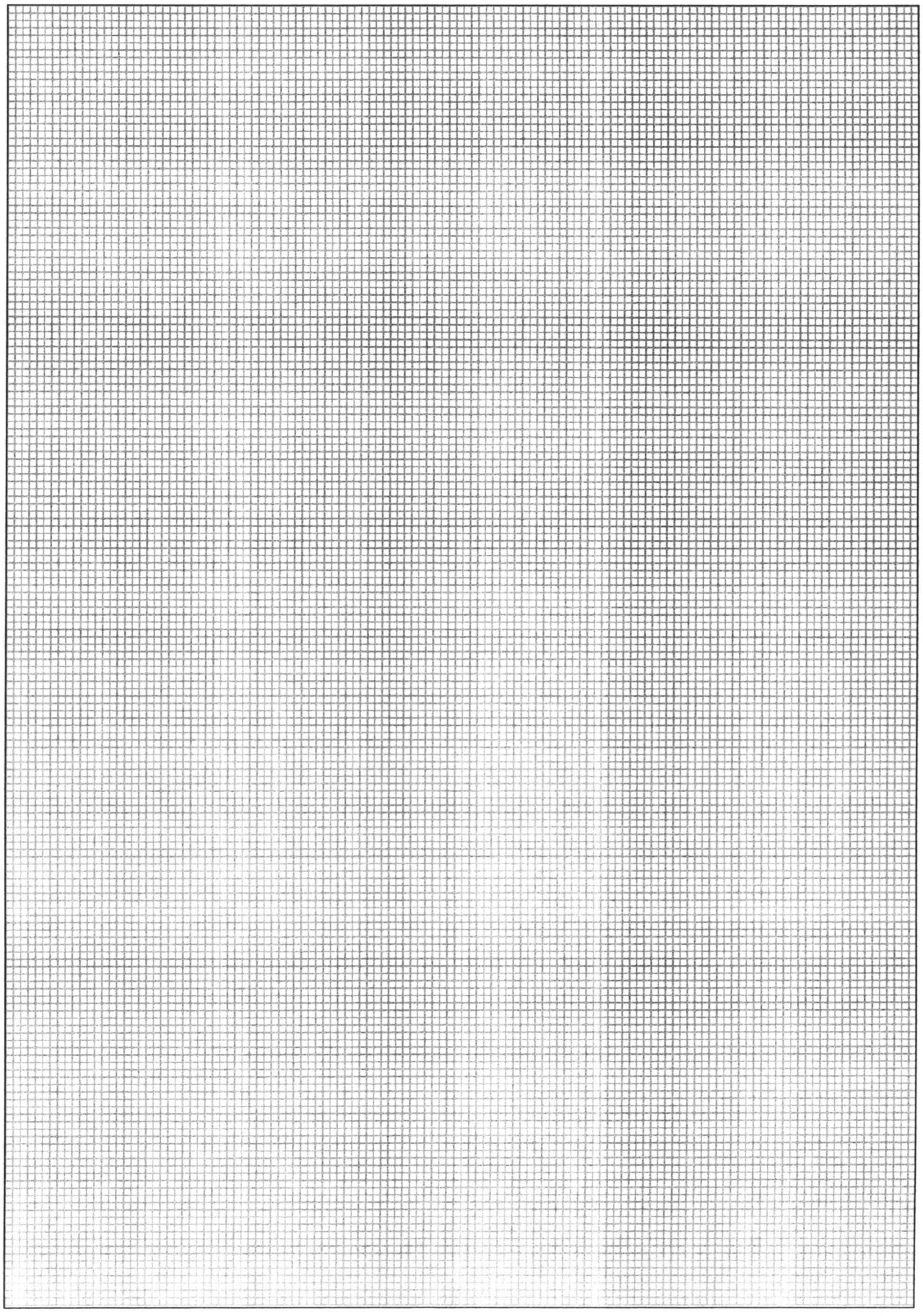

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V.3. ENTHALPIES OF REACTIONS. APPLICATION OF HESS'S LAW

In this experiment, the heat of formation of ammonium sulfate from ammonia and sulfuric acid will be evaluated. The heats of intermediary steps will be used and finally the Hess Law will be applied.

This experiments belongs to thermochemistry, the part of thermodynamics that is concerned with the heat effects attending processes that give rise to changes of phase and changes in composition.

Several reactions will be experimentally produce, the enthalpy of them will be calculated and using the obtained data and Hess's Law, the enthalpy of an unknown chemical process will be evaluated.

Law of constant heat summation – or Hess's Law is usually stated in the form: the resultant heat change, at constant pressure or constant volume, in a given chemical reaction is the same whether it takes place in one or several stages. This law is an extremely useful because it permits the calculation of ΔH or ΔE for reactions for which these quantities cannot be directly measured. An example will make this clear. We required to know ΔH for the reaction:

(x) $2NH_3(g) + H_2SO_4(l) \rightarrow (NH_4)_2SO_4(s)$ $\Delta H_x = ?$

We cannot determine this quantity directly simply because the reaction will not go (it's very hard to work in three aggregation states and the effect of this reaction has a great value).

The quantity can, however, be calculated from heat of other four reactions:

- the dissolution of gaseous ammonia in water (V.3-1);
- the dilution of liquid sulfuric acid in water (V.3-2);
- the neutralization reaction of aqueous solution of sulfuric acid with ammonium hydroxide (V.3-3);
- the water dissolution of solid ammonium sulfate (V.3-4).

(V.3-1) $NH_3(g) + H_2O(l) \rightarrow NH_4OH(aq)$ $\Delta H_1 = -8350$ cal/mole

(V.3-2) $H_2SO_4(l) + H_2O(l) \rightarrow H_2SO_4(aq)$ ΔH_2

(V.3-3) $H_2SO_4(aq) + 2NH_4OH(l) \rightarrow (NH_4)_2SO_4(aq) + 2H_2O(l)$ ΔH_3

(V.3-4) $(NH_4)_2SO_4(s) + H_2O(l) \rightarrow (NH_4)_2SO_4(aq)$ ΔH_4

According to Hess's Law, the enthalpy of (x) reaction can be calculated with the relation:

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$$\boxed{\Delta H_x = 2\Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4} \quad \text{(V.3-5)}$$

METHOD

A convenient way for determining the heats of the reactions is *adiabatic calorimetry*. An adiabatic calorimeter with unknown heat capacity will be used.

The heat capacity of the system, if not known, must be determined. A direct method, which depends on the assumption of the constancy of heat capacities over a small range of temperature, is to measure the temperature rise ($\Delta T_1 = T_1 - T_0$) produced by the dissipation of a measured quantity of electrical energy.

$$C_p (or \cdot C_v) = \frac{W_{el}}{T_1 - T_0} \quad \text{(V.3-6)}$$

at constant pressure or at constant volume, respectively.

The electrical work produced during the heating of the system is:

$$W_{el} = U \cdot I \cdot t \quad \text{(V.3-7)}$$

where U represents the current potential (measured in volts – V), I is the current intensity (measured in amperes – A) and t is the time of passing the current through the system (measured in seconds – s). The unit of electrical work is Joule (J). If we want to express the electrical work in calories (1 cal=4.185 J), we will use the relation:

$$W_{el} = 0.239 \cdot U \cdot I \cdot t \quad \text{(V.3-8)}$$

Combining the equations (V.3-6) and (V.3-8) one can obtain:

$$C_p = \frac{0.239 \cdot U \cdot I \cdot t}{T_1 - T_0} \quad \text{(V.3-9)}$$

But C_p is a total heat capacity of a system which is formed from the water and calorimetric vessel with its accessories:

$$C_p = C_{H_2O} + A \quad \text{(V.3-10)}$$

where C_{H2O} represents the heat capacity of water and A is heat capacity of the calorimetric vessel with its accessories.

The heat capacity of water can be easily calculated:

$$C_{H_2O} = m_{H_2O} \cdot c_{H_2O} = \rho_{H_2O} \cdot V_{H_2O} \cdot c_{H_2O} \quad \text{(V.3-11)}$$

where:

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- m_{H2O} = mass of the water (g);
- c_{H2O} = specific heat of the water at constant pressure (c_{H2O} = 1 cal/gK);
- ρ_{H2O} = density of water (ρ_{H2O} = 1 g/ml);
- V_{H2O} = the volume of water added into the calorimeter (V_{H2O} = 500 ml).

From equations (V.3-9), (V.3-10) and (V.3-11) one can obtain A:

$$A = \frac{0.239 \cdot U \cdot I \cdot t}{T_1 - T_0} - \rho_{H_2O} \cdot V_{H_2O} \cdot c_{H_2O} \qquad \text{(V.3-12)}$$

The heats of the involved reactions will be calculated using the determined C_p of a system, the temperature variations recorded during each process and the involved mole number of the reactant.

$$\Delta H = \frac{Q}{n} = \frac{C_p \cdot \Delta T}{n} \qquad \text{(V.3-13)}$$

APPARATUS AND CHEMICALS

- Adiabatic calorimeter (Dewar flask), stirrer – heater (heating coil) unit complete with motor and power cord, dc power – supply unit for heater, ampermeter, voltmeter, precision calorimeter thermometer (Beckmann), magnifying thermometer reader, stopwatch, one 25- and one 500-ml cylinders, 2-ml pipette, analytical balance;
- Distilled water, H_2SO_4 94%, NH_4OH (l), $(NH_4)_2SO_4$ (s).

EXPERIMENTAL

The reaction is carried out in a circuit with an adiabatic calorimeter shown in figure V.3-1.

The calorimeter is a vacuum bottle (Dewar flask) containing a Beckmann thermometer, a motor – driven stirrer and heating coil of precisely known electrical resistance.

Procedure

Place roughly 500 ml of distilled water in the calorimeter and introduce the stirrer – heater unit and thermometer. Make the electrical connections as shown in figure V.3-1. Adjust the thermometer (adjusting the thermometer will be made only by the teacher). Turn on the stirrer. Commence reading the temperature on the thermometer, readings being made every minute till the temperature remains constant. After the reaching of a constant value of temperature (say T_0), turn on the current to the heater (electrical resistance) and pass the current for exact time (3 minutes). During the passing electrical

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current, note the values for the electrical potential and the current intensity recorded on voltmeter and miliampermeter respectively.

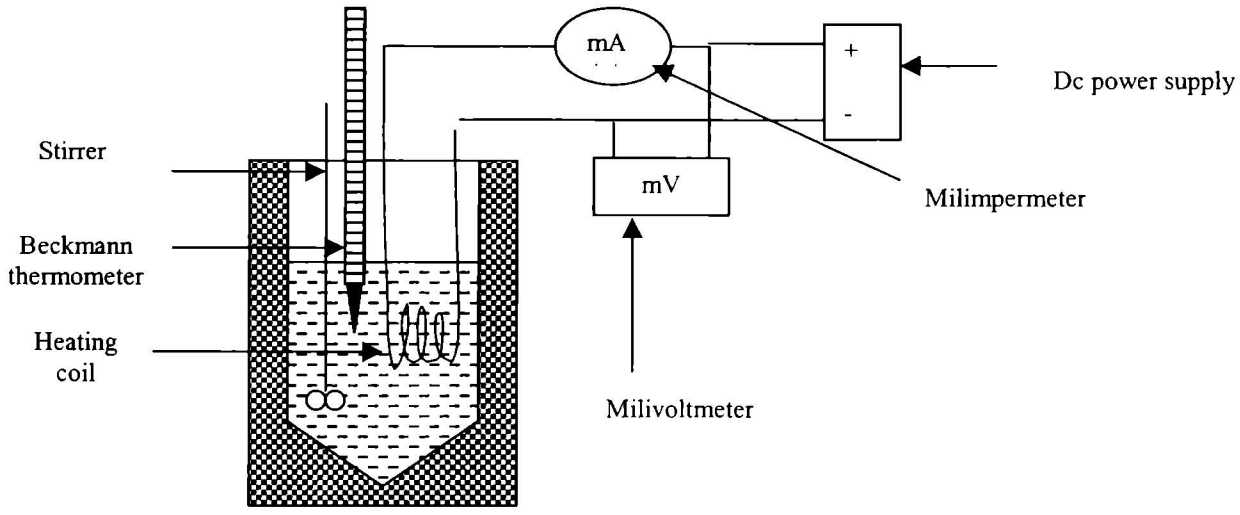

Figure V.3-1 Adiabatic calorimeter scheme

After three minutes, turn off the current to the heater. During the heating (3 min) and after that, take readings of temperature, minute by minute, until the highest temperature is reached and furthermore to the constant value of temperature (T_1).

In order to avoid working with gaseous ammonia, the first process will not be studied. So that the enthalpy of the first reaction will be given (ΔH_1 = -8350 cal/mole).

When the thermal equilibrium is established (T_1), take 1.5 ml of H_2SO_4 94% (ρ = 1.83 g/ml) and pipette into the calorimeter. Again take readings of the temperature, minute by minute until the constant temperature (T_2). When T_2 is reached, take 15 ml of NH_4OH (l) by means of a cylinder, add it into the calorimeter, and make reading of temperature till the constant temperature (T_3).

When the studying of the third process is finished, stop the stirrer and empty the calorimeter. Place roughly another 500 ml of distilled water, turn on the stirrer motor and commence reading temperature on the thermometer (every minute) till a constant value (T_0'). Then weigh 3 g of $(NH_4)_2SO_4$ by means of a analytical balance and add the amount into the calorimeter. Again take readings of temperature, minute by minute, until the constant value of it is obtained (T_4). After that, empty the calorimeter and start computing the results.

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CALCULATIONS

- *Determine the water equivalent (heat capacity) of a calorimetric system using the relation (V.3-9):*

$$C_p = C_{H_2O} + A = \frac{0.239 \cdot U \cdot I \cdot t}{T_1 - T_0}$$

- *Determine the enthalpy of reaction (V.3-2) using relation (V.3-14):*

$$\Delta H_2 = \frac{Q_2}{n_{H_2SO_4}} = \frac{C_p \cdot \Delta T_2}{n_{H_2SO_4}} \qquad \text{(V.3-14)}$$

where $C_p$is heat capacity of the system, $\Delta T_2 = T_2 - T_1$, n_{H2SO4} = moles number of sulfuric acid which can be calculated from the concentration (94%), density (1.83 g/ml) and used volume (1.5 ml);

- *Determine the enthalpy of neutralization (reaction V.3-3) using the relation (V.3-15):*

$$\Delta H_3 = \frac{Q_3}{n_{(NH_4)_2SO_4}} = \frac{C_p \cdot \Delta T_3}{n_{(NH_4)_2SO_4}} = \frac{C_p \cdot \Delta T_3}{n_{H_2SO_4}} \qquad \text{(V.3-15)}$$

where $\Delta T_3 = T_3 - T_2$

- *Determine the enthalpy of reaction (V.3-4) – the dissolution of $(NH_4)_2SO_4$ (s):*

$$\Delta H_4 = \frac{Q_4}{n_{(NH_4)_2SO_4}} = \frac{C_p \cdot \Delta T_4}{n_{(NH_4)_2SO_4}} \qquad \text{(V.3-16)}$$

where $\Delta T_4 = T_4 - T_0'$.

! Be careful at the signs of the above enthalpies.

- *Determine the enthalpy of reaction (x) using the relation (V.3-5):*

$$\Delta H_x = 2\Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4$$

- *Present in tabular form the obtained results.*

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Table V.3-1 Experimental data

Reaction	Moles number of reactant (mole)	ΔT (K)	ΔH	
			(cal/mole)	(kJ/mole)
1	-	-	-8350	-34.90
2				
3				
4				
x				

CONCLUSIONS AND DISCUSSIONS

- Name the type of the studied reactions;
- Which processes are exothermic and which are endothermic?
- The calorimetric method is also useful to determine the heats of ionic reaction and heats of solution.

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V.4. HEAT OF VAPORIZATION

In this experiment, the heats of vaporization of some volatile liquids will be determined by means of calorimetry. In addition, the entropy of vaporization of volatile liquids will be calculated.

Lets consider, for example, the evaporation of one liquid component C to vapors, a change in state that can be symbolized by the equation:

$$C^l \Leftrightarrow C^g$$

It was experimentally found that when this process takes place at constant pressure and constant temperature, let say 100 ^{0}C and one atmosphere (for C = water), the heat that must be supplied is 9720 calories/mole; this is the change in enthalpy (Δ^vH) associated with the process of vaporization.

The definition of enthalpy is:

$$H = E + PV \qquad \text{(V.4-1)}$$

By differentiating the equation (V.4-1) one can obtain:

$$dH = dE + PdV + VdP \qquad \text{(V.4-2)}$$

and at constant pressure:

$$dH = dE + PdV \qquad \text{(V.4-3)}$$

For a finite variation:

$$\Delta H = \Delta E + P\Delta V \qquad \text{(V.4-4)}$$

The work accompanying such an evaporation, if carried out reversibly, will equal PΔV, in which expression ΔV is the difference between the volume of the vapor and that of the liquid: $\Delta V = V^g - V^l$. To obtain an excellent approximation for ΔV, we can neglect the volume of the liquid compared with that of the vapor, implying that the work is nearly equal to the pressure – volume product of the vapors. Assuming further that the vapor is an ideal gas, we can write that:

$$W = P\Delta V = RT \qquad \text{(V.4-5)}$$

The molar heat of vaporization of a liquid is defined as the quantity of heat required to change one mole of the liquid to the vapor state.

The molar heat of vaporization can be determined by means of an adiabatic calorimeter. The used relation is:

$$\Delta^v H = \frac{Q}{n} = \frac{C \times \Delta T^*}{n} \qquad \text{(V.4-6)}$$

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where C is heat capacity of the system (have the given value 750 cal / K); ΔT^* is corrected temperature measured during the vaporization process and n is the moles number of evaporated substance.

The molar heat of vaporization can be used for the calculation of the molar entropy of vaporization of substance at its normal boiling point (T_0):

$$\Delta^v S = \frac{\Delta^v H^0}{T_0} \qquad \text{(V.4-7)}$$

The relation (V.4-7) represents Trouton's Law when $\Delta^v S \cong 21$ cal / mole K. In effect, the law stated that the increase in entropy on the vaporization of a liquid at its normal boiling point is approximately $\Delta^v S \cong 21$ cal / mole K for non - associated liquids.

METHOD

The heats and entropy of vaporization will be determined by means of an adiabatic calorimeter, with known heat capacity (50 cal / K) will be used.

APPARATUS AND CHEMICALS

- Adiabatic calorimeter (Dewar), inner vessel in coil shape (evaporation vessel) with a feeding tap, stirrer complete with motor and power cord, precision calorimeter thermometer (Beckmann), magnifying thermometer reader, stopwatch, vacuum pump, 5 ml pipette, rubber pipetting bulb;
- Chemicals: etilic ether, acetone, chloroform, carbon tetrachloride and methanol.

EXPERIMENTAL

The scheme of experimental setup is presented in figure V.4-1.

Fill the evaporation vessel with an exact volume of volatile liquid (take the value of the volume from the table 4.1), by using the rubber pipetting bulb. Than close the feeding tap and start the stirrer. Adjust the thermometer (adjusting the thermometer will be made only by the teacher). Commence reading the temperature on the thermometer, readings being made every minute till the temperature remains constant. After the reaching of a constant value of temperature, make the connection between evaporation vessel and vacuum pump and then start the pump. The temperature of the water in the calorimeter will now begin to decrease. Again take readings of temperature, minute by minute until the

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lowest temperature is reached, a point which must be carefully noted. The temperature will now begin to rise slowly and readings at intervals of minute must again be made for about five minutes. After that disconnects the vacuum pump from the plug, open all the taps, and stop the stirrer. These complete the series of observations.

The first experiment should be repeated for all volatile substances presented in table V.4-1.

The pipette which will be used need to be perfectly dried (do not wash the pipette between experiments).

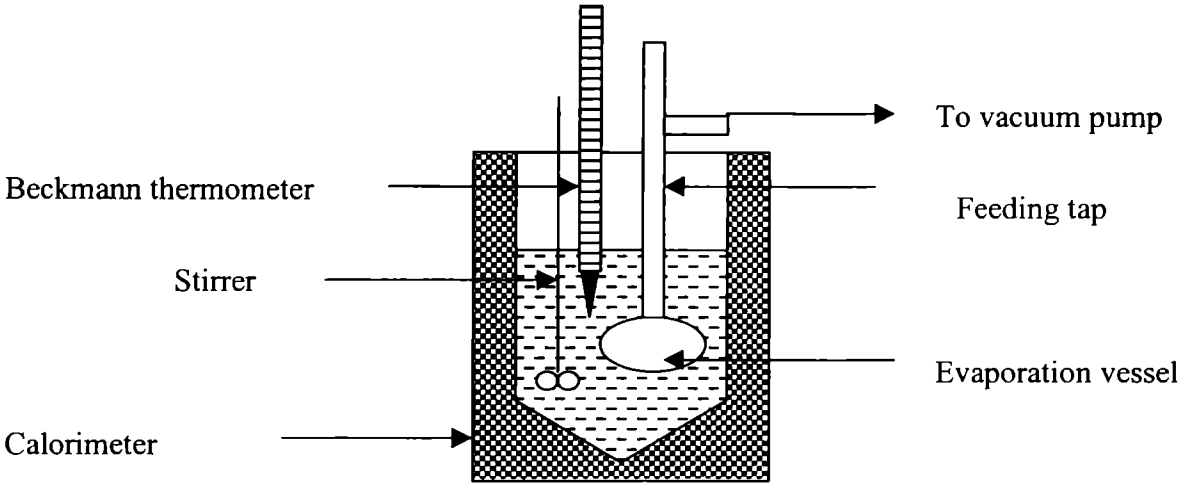
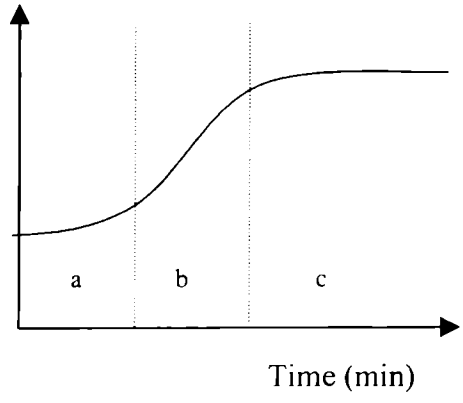


Figure V.4-1 Adiabatic calorimeter

CALCULATIONS

- *Determine the temperature variations recorded on the evaporation of each volatile substance and make a correction of these values if necessary:*

$$\Delta T^* = \Delta T_p - t_p\left[\left(\frac{\Delta T}{\Delta t}\right)_i + \left(\frac{\Delta T}{\Delta t}\right)_f\right] \qquad (4.8)$$



Where:

ΔT^* = corrected temperature variation;

ΔT_p = temperature variation in principal period (b);

t_p = time of principal period;

$(\Delta T/\Delta t)_i$ = temperature variation in time interval of initial period (a);

$(\Delta T/\Delta t)_f$ = temperature variation in time interval of final period (c).

- *Calculate the mole number of each evaporated substance using the data from the table V.4-1.*

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$$n = \frac{m}{M} = \frac{\rho V}{M} \qquad \text{(V.4-9)}$$

where n represents the mole number of each substance, ρ is the liquid density, V is the volume used at evaporation and M represents the molecular mass of the substance.

- *Determine the values of the molar heats of evaporation using equation (V.4-6):*

$$\Delta^v H = \frac{Q}{n} = \frac{C \times \Delta T^*}{n} \qquad \text{(cal / mole)} \qquad \text{where C = 750 cal / K.}$$

- *Determine the values of molar entropy of vaporization of each liquid at its normal boiling point* (take the values for T_0 from the table V.4-1) *using equation (V.4-7):*

$$\Delta^v S = \frac{\Delta^v H^0}{T_0} \qquad \text{(cal / mole K)}$$

- *Present in tabular form the obtained results.*

Table V.4-1 Obtained data

		$(C_2H_5)_2O$	$(CH_3)_2CO$	$CHCl_3$	CCl_4	CH_3OH
Boiling point	**t_0 (^{0}C)**	34.6	58.3	61.3	76.6	64.7
	T_0 (K)					
V (ml)		3	3	1.5	1.5	1.5
ρ (g / ml)		0.7135	0.7920	1.4880	1.5390	0.7915
n (mole)						
ΔT^* (K)						
ΔH_v (cal / mole)						
ΔS_v (cal / mole K)						

CONCLUSIONS AND DISCUSSIONS

- Interpret the obtained values for the molar entropy of vaporization regarding Trouton's Law;
- Knowledge of the molar heat of vaporization is useful in computing the ebulioscopic constant or the molar boiling point elevation.

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V.5. HEAT OF COMBUSTION

In this experiment a bomb calorimeter is employed in the determination of the heat of combustion of an organic substance such as cellulose $(C_6H_{12}O_5)_n$. The caloric power of cellulose at constant temperature and pressure is q_{cel}. Benzoic acid will be used, as standard substance, for the determination of heat capacity of the calorimetric system. The involved reactions are:

$$C_6H_5COOH + \frac{13}{2}O_2 \rightarrow 7CO_2 + 3H_2O$$

$$(C_6H_{12}O_5)_n + \frac{13n}{2}O_2 \rightarrow 6nCO_2 + 6nH_2O$$

In thermochemical calculations standard heats of formation provide many useful data. The standard heats of formation of many organic compounds may be calculated from knowledge of the heat of combustion of the compound and the standard heats of formation of carbon dioxide and water. These data are not restricted in usefulness to the directly – measured combustion reactions, for by combining several such reactions according to Hess's Law one can deduce the heats of the other reactions.

METHOD

A convenient way to determining the heats of combustion is with a bomb calorimeter in which the substance is burnt in an atmosphere of compressed oxygen in a closed vessel. In this way the reaction is carried out at constant volume at the heat evolved is therefore equal to the decrease in the internal energy of the system.

The heat of combustion at constant pressure, the enthalpy change of the reaction, may then calculated from the relation:

$$\Delta H = \Delta E + \Delta nRT$$

where Δn is the increase in the number of moles of gas during the reaction.

APPARATUS AND CHEMICALS

- Bomb calorimeter complete, quasiadiabatic calorimeter, stirring motor with power cord, one set of electrical leads which connect to bomb, precision calorimetric thermometer (Beckmann

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thermometer), stopwatch (stopclock), a cylinder of compressed oxygen fitted with a needle valve and pressure gauge.

- Benzoic acid, cellulose.

EXPERIMENTAL

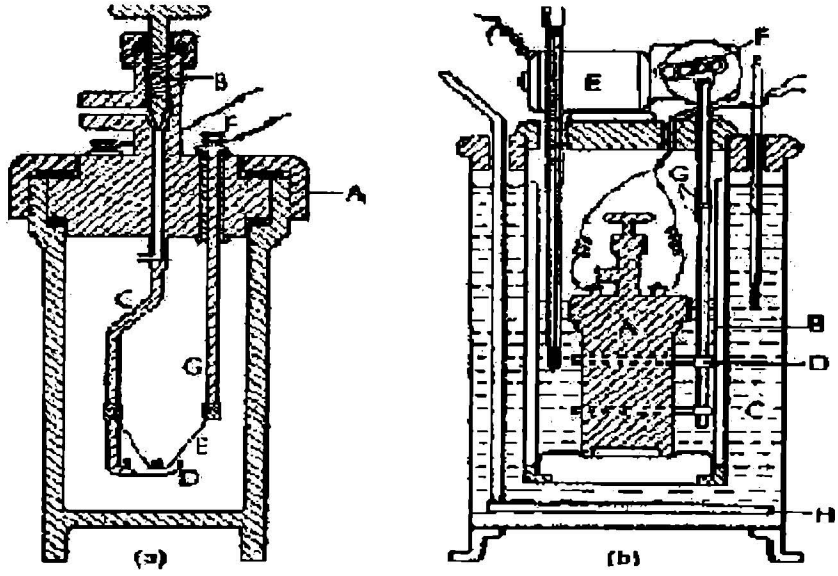

Figure V.5-1 The bomb calorimeter

a) construction of the bomb

b) arrangement of the apparatus in the calorimeter

The bomb (fig. V.5-1 a) consists of a stainless steel pressure vessel. The lid is held in place by a strong locking – nut, A, and rendered gas – tight by washers. Oxygen is charged into the bomb through the needle – valve, B. A rod, C, supports a crucible of silica or platinum to contain the substance which is to be burnt. Combustion is initiated by means of a fine platinum or iron wire, E, which is heated momentarily to redness by passage of an electric current, the current being introduced through an insulated terminal, F, and the rod C (which is in electrical connection with the lid).

Fig. V.5-1 b shows the rest of the apparatus. The bomb A is placed in water in a stainless steel calorimeter vessel, B, which is surrounded by a double – walled copper water – jacket, C. The water in the inner vessel is stirred automatically by a reciprocating stirrer, D, driven by a small electric motor, E, and reduction gear and eccentric, F. In order to minimize heat conduction along the stirrer, an ebonite rod, G, is interposed between the upper and lower parts. The top of the apparatus is closed by

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two wooden lids which are provided with two holes to take a Beckmann thermometer for the inner vessel, an ordinary thermometer graduated in tenths of degree for the outer water – jacket. The later should be provided with a simple stirrer, H.

The water – equivalent of the calorimeter (or heat capacity of calorimetric system) must be determined by burning a known weight of a substance of well – established heat of combustion. Pure benzoic acid is usually used, its heat of combustion being 6318 cal/g.

The same amount of water must, of course, be used in the calorimeter for the experiment with benzoic acid as with the test substance.

Procedure

The substance to be burned is first compressed into a pellet and, after being weight, is placed in the crucible D. A piece of fine iron wire (with characteristic: R = 0.18 Ω/cm and heat of combustion 0.845 cal/cm) is measured and its ends connected with the rods C and G. The middle portion of the wire should be twist around the pellet of compressed substance. The cover of the bomb is tightly screwed down with the help of a large spanner, the bomb being meanwhile fixed with its holder. The bomb is now ready to be filled with oxygen.

A cylinder of compressed oxygen fitted with a needle valve and pressure gauge is connected to the valve B by the metal pipe provided with the calorimeter. Open the valve B slightly, then the main cylinder valve, and then cautiously open the slow – release valve attached to the cylinder and allow oxygen to stream slowly into the bomb until the pressure registered on the manometer is 20 – 25 atm. Now close the valves and disconnect the tube from the bomb. If there is any leakage of gas it will generally be detectable by a slight hissing sound.

The charged bomb is lowered cautiously into the water of the calorimeter. Flexible wire is then connected to the terminals, and the lid of the calorimeter placed in position. Insert the Beckmann thermometer into the calorimeter and set the stirrer in motion at such a rate that it rises and falls about once per second. After the bomb has been in the water about five minutes, commence reading the temperature on the thermometer, readings being made every minute for about ten minutes (or till the temperature remains constant). At the tenth minute fire the ignition wire by means of a switch key, in series with the mains and rheostat – a suitable potential must be found by preliminary experiments. The iron wire will thereby be caused to burn and will ignite the substance in the crucible. The temperature of the water in the calorimeter will now begin to rise rapidly. Again take readings of the temperature, minute by minute (it will probably be impossible to make a reading at the first minute after ignition), until the highest temperature is reached, a point which must be carefully noted. The temperature will

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now begin to fall slowly, and readings at intervals of a minute must again be made for about ten minutes. These complete the series of observations. The bomb is removed from the calorimeter and carefully dried. The needle valve B is slowly opened so as to allow the gases to escape from the bomb. When the pressure has fallen down again to that of the atmosphere the cover is removed and the interior of the bomb cleaned and dried. Any of the iron wire has not been oxidized should be measured and the length subtracted from the originally taken. The same experiment should be repeated for the cellulose.

CALCULATIONS

- *Determine the temperature variation and make the correction of this variation (in the same manner as presented at "Heat of vaporization")*

  The same correction has to be made for the combustion of benzoic acid and cellulose.

- *Determination of heat capacity of calorimetric system*

  When we make the combustion of benzoic acid there are three quantities of heat which are produced:

  - Q_1 – the heat of combustion of benzoic acid

    1g benzoic acid.....$q_1 = 6318$ cal

    $m_{benzoic\ acid}$.....Q_1 $\rightarrow$ $Q_1 = 6318 \times m_{benzoic\ acid}$ (cal)

  - Q_2 – the heat of combustion of iron wire

    $Q_2 = 0.845 \times l_{iron\ wire}$ (cal)

    where $l_{iron\ wire}$ is the length of the iron wire.

  - Q_3 – the Joule effect which appears when we connect flexible wires to the terminals

    $Q_3 = 0.239\ Rit^2$ (cal)

    where R is resistance of iron wire, I is the intensity of the current and t is the combustion time.

  Because the values of Q_2 and Q_3 are very small comparatively with the value of Q_1 we will neglect them in our calculations. The heat capacity of the system can be calculated with the relation:

$$C_{system} = \frac{Q_1 + Q_2 + Q_3}{\Delta T_1^*} \cong \frac{Q_1}{\Delta T_1^*} \text{ (cal / K)} \qquad \text{(V.5-1)}$$

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where ΔT_1^* is the corrected temperature variation recorded at combustion of benzoic acid.

- *Determination the heat of combustion of cellulose*

$$Q_{cellulose} = C_{system} \times \Delta T_2^* \quad \text{(cal)} \qquad \text{(V.5-2)}$$

where ΔT_2^* is the corrected temperature variation recorded at combustion of cellulose.

- *Determination the caloric power of cellulose*

$$q_{cellulose} = \frac{Q_{cellulose}}{m_{cellulose}} \quad \text{(cal / g)} \qquad \text{(V.5-3)}$$

- *Present the results in tabular form*

Table V.5-1 Experimental data

substance	m (g)	ΔT^* (K)	q (cal / g)	C_{system} (cal / K)
Benzoic acid			6318	
Cellulose				

CONCLUSIONS AND DISCUSSIONS

- explain the connection between the heat of combustion and the chemical structure of the studied substances;
- volatile liquids can be burned by enclosing them in a gelatin capsule of known weight and calorific value;
- the method of calculating the heat of combustion from the corrected temperature rise will be apparent;
- bomb calorimetry is applicable to a wide variety of substances, but complications arise for substances containing sulfur, nitrogen, phosphorus etc since one mist know the products formed in the reaction.

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V.6. THERMAL DECOMPOSITION OF CALCIUM CARBONATE

This experiment is concerned with the heterogeneous equilibrium between two phases in a system with three components. The particular system to be studied is: $CaCO_3$ – CaO – CO_2. The enthalpy of decomposition of $CaCO_3$ will be determined by manometric measurements.

The equilibrium equation is:

$$CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$$

The study of this equilibrium is presented in theoretical part of this book (chapter III. c)

According to the equation (III. 26):

$$\frac{d \ln K_x}{dT} = \frac{d \ln K_P}{dT} = \frac{d \ln P_{CO_2}}{dT} = \frac{\Delta H}{RT^2}$$

where ΔH represents the enthalpy of dissociation for $CaCO_3$. After the integration of equation (III. 26), we obtain:

$$\ln P_{CO_2} = -\frac{\Delta H}{R} \cdot \frac{1}{T} + const. \qquad \text{(V.6-1)}$$

or

$$\log P_{CO_2} = -\frac{\Delta H}{2.303 \cdot R} \cdot \frac{1}{T} + const. \qquad \text{(V.6-1')}$$

We can see that in a case when ΔH is independent of temperature, then a plot of $\ln P_{CO_2}$ $\left(or \cdot \log P_{CO_2}\right)$ versus 1/T would be a straight line, and from the slope (tgα) we can determine the value of ΔH:

$$\Delta H = -R \cdot tg\alpha \qquad \text{(V.6-2)}$$

or

$$\Delta H = -2.303 \cdot R \cdot tg\alpha \qquad \text{(V.6-2')}$$

METHOD

In the case of heterogeneous equilibria of dissociation (particularly – the system: $CaCO_3$ – CaO – CO_2), a certain value of pressure function of temperature will be established, according to the law of chemical equilibrium. The experimental studies of thermal decomposition of solids with appearance of a gas phase can be manometricaly followed by introducing of an amount of solid in an evacuated ampoule connected with a manometer.

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APPARATUS AND CHEMICALS

In the electric oven (O) is introduced a quartz ampoule (A) that contains a certain amount of solid $CaCO_3$. At the same level with the ampoule is placed a Pt-Pt (Rh) thermocouple (T) in the connection with a milivoltmeter (mV). By means of the stopcock (S1) the ampoule is connected with the vacuum pump (VP) and with the mercury manometer (M).

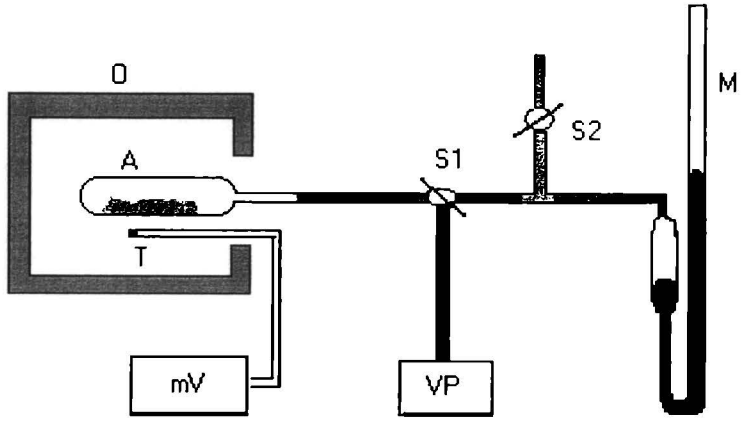

Figure V.6-1 Scheme of the experimental device.

EXPERIMENTAL

With help of the vacuum pump and the stopcock S1, the entire installation is evacuated. The connection with the vacuum pump is closed and starts the heating of the ampoule with $CaCO_3$. The oven is equipped with an electronic device that allows adjusting the heating rate. The temperature in the oven is read at the milivoltmeter that is graduated in mV as well as in Celsius degree. The temperature detector is a Pt-Pt (Rh) thermocouple. The dissociation of calcium carbonate begins at about 500^0C. From this temperature we can observe the rise pressure at mercury manometer. For each value of the temperature is established a determined value of the pressure of dissociation (Pressure of dissociation is an intensive property and therefore is independent from the mass of $CaCO_3$ introduced in the ampoule as well as from the volume of the system).

Because the dissociation process is a reversible one, we can study the equilibrium in both ways: the decomposition of $CaCO_3$ (heating process) and the reformation of calcium carbonate (cooling process). When the experiment is cautiously achieved, the experimental values must be reproducible.

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CALCULATIONS

- *Determine the values of pressures at different temperatures (start recording at 500^{0}C and note the values of pressures from 20 to 20^{0}C);*
- *Calculate the ln P and 1/T then plot the obtained values for lnP versus 1/T;*
- *Determine the slope of the graph and calculate the* ΔH using the equation (V.6-2):

$$\Delta H = -R \cdot tg\alpha \qquad \text{(V.6-2)}$$

- *Present in tabular form the obtained results.*

Table V.6-1 Experimental data

t (^{0}C)	T (K)	1/T (K^{-1})	p (mm Hg)	ln p	tgα (K)	ΔH (cal/mole)
700						
720						
740						
760						
780						
800						
820						
840						
860						
880						
900						
920						
940						
960						
980						
1000						

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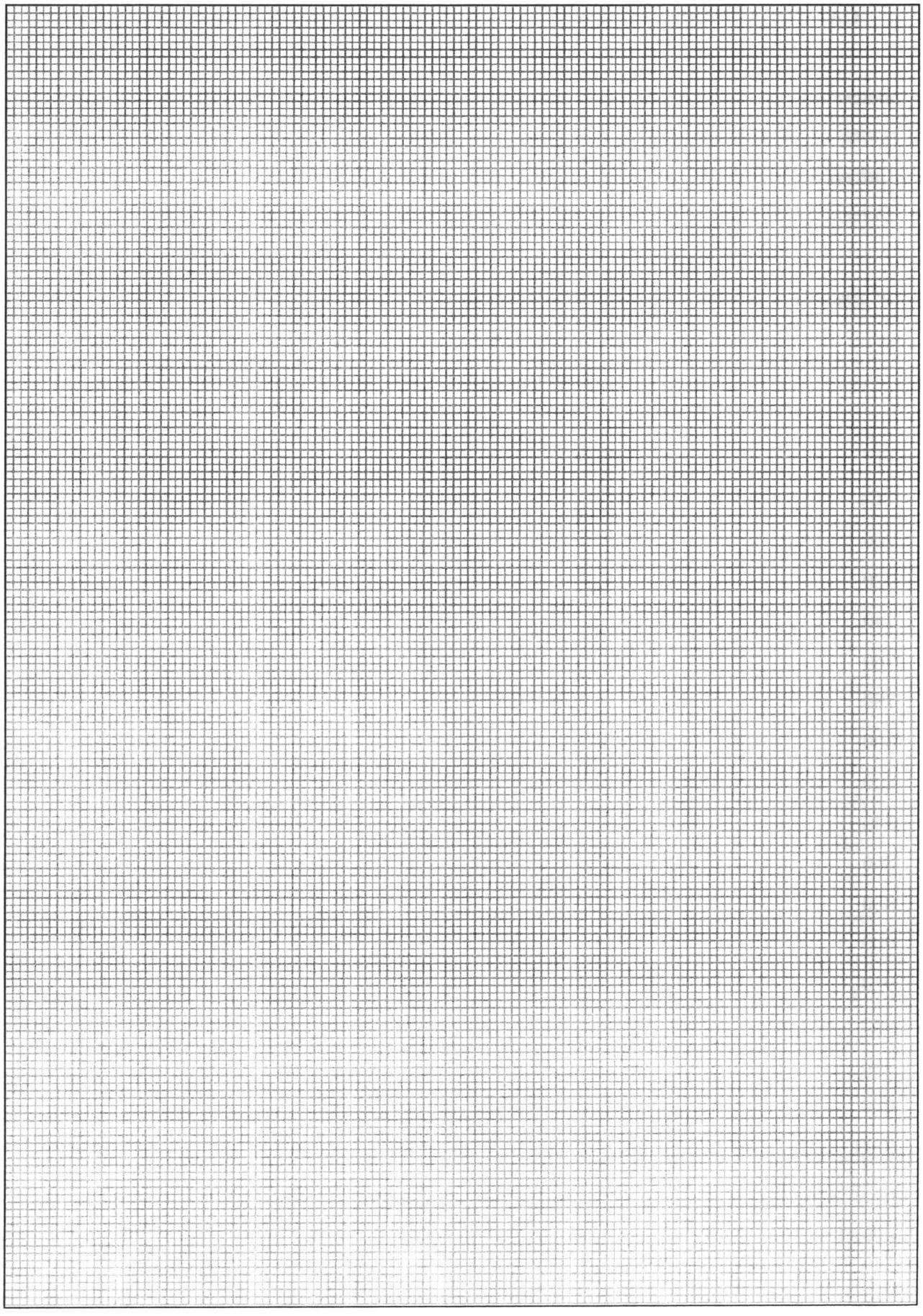

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V.7. CHEMICAL EQUILIBRIUM IN GASES

METHOD

A particular case among chemical equilibria is represented by reactions in gas phases. An interesting example is the reaction:

$$CO_{2(g)} + H_{2(g)} \Leftrightarrow H_2O_{(g)} + CO_{(g)}$$

The position of chemical equilibrium cannot be establish by simple measurements of total pressures because $\Delta\nu = 0$. Between experimental methods used for the study of this chemical equilibrium we shall present the Langmuir method, known as the method of hot catalyst.

The principle of the method consists in the fact that it is not necessary to bring the entire amount of gases at equilibrium temperature but only a part of it, which is in contact with a platinum wire. Platinum wire is heated at sufficient high temperature in order to carbon dioxide and hydrogen to react. Because in the vicinity of hot wire the decrease of temperature is high a diffusion process will take place that determines the reaction products displace in a place of equilibrium cell where practical the reaction is not possible. After some time the entirely quantity of the gas will have the same composition as in the vicinity of hot catalyst.

The calculation of equilibrium constant is practical reduced to the analysis of gas mixture, process that can be solved by different methods. It is easy to observe that is sufficient to know the partial pressure of a component, partial pressures of the other components being determined from the reaction stoechiometry.

For the studied system lets note by a and b the partial pressures of CO_2 and H_2 respectively; in this case the equilibrium constant will be:

$$K_P = \frac{P_x^2}{(a - P_x)\cdot(b - P_x)} \qquad \text{(V.7-1)}$$

where P_x represents the partial pressure of water vapors respectively the partial pressure of CO.

The simplest method for the determination of partial pressure of water vapors is to condense the vapors.

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APPARATUS AND CHEMICALS

The working cell c – a glass vessel with a volume about 500 cm^3 – is connected by a glass capillary with mercury manometer M (see figure V.7-1).

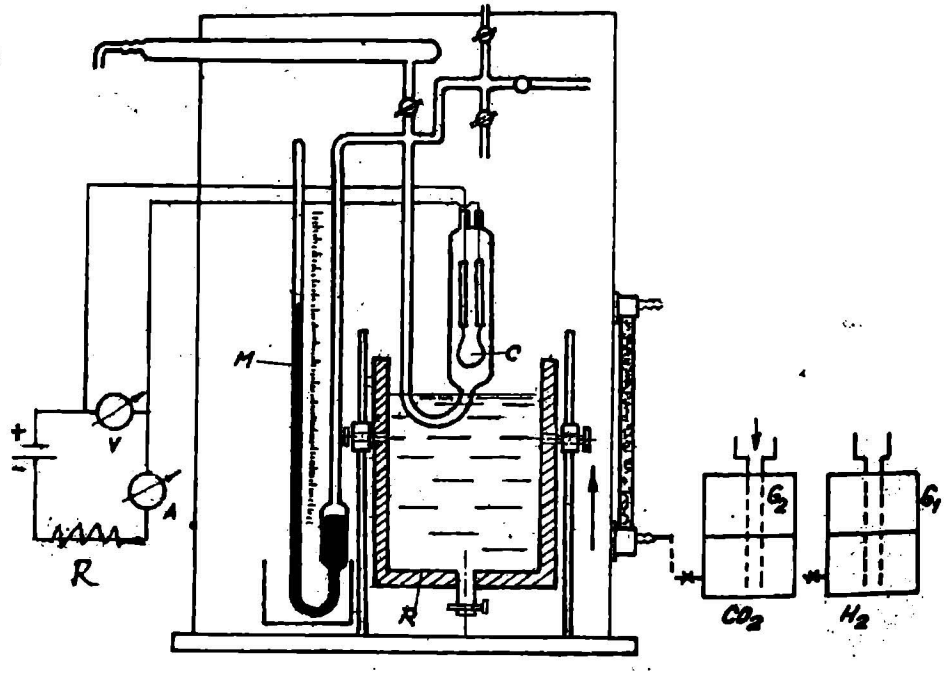

Figure V.7-1 The scheme of the experimental apparatus

The platinum wire (with the length of 12 cm and 0.4 mm thickness) is fixed at the upper end of the cell by means of two wolfram electrodes. Using of two gas-meters is performed the supply of the equilibrium cell with carbon dioxide and hydrogen.

The working gases, CO_2 and H_2, have high purity (about 99%).

EXPERIMENTAL

The working cell is introduced in a metallic bath R (having double insulated walls). By using of two steel rods the position of working cell can be adjust. The metallic bath is filled with distilled water heated up to about 70 – 80^0C. The value of temperature is exactly measured and should remain constant during the entire experiment. The cell is then evacuated and CO_2 and H_2 from the gas-meters are

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carefully introduced up to a pressure of about 200 mm Hg. The electric circuit is then closed and the current is adjusted at about 6 A, that correspond to light yellow color of platinum wire. The electric intensity and voltage values and the values of gas pressures are from time to time measured. After a period of about 15 minutes, the entirely quantity of gas riches the equilibrium value. At this moment the electric supply is stopped, the hot water from R is evacuated and the bath is then filled with ice water.

CALCULATIONS

- *Knowing that at 0^0C, the pressure of water vapor is 4.6 mm Hg, the measured P_0 will be,*

$$P_0 = \left[\left(P_{CO} + P_{CO_2} + P_{H_2}\right) \times \frac{273}{353} + 4.6\right] mmHg \qquad \text{(V.7-2)}$$

if the initial temperature was 80^0C (in other cases the exact value is noted).

- *For the pressure measured at 80^0C we have:*

$$P_{80} = P_{CO} + P_{CO_2} + P_{H_2} + P_{H_2O} = a + b \qquad \text{(V.7-3)}$$

- *`Finally we will obtain:*

$$P_x = P_{H_2O} = a + b - \frac{353}{273} \cdot P_0 + 4.6 \cdot \frac{353}{273} \qquad \text{(V.7-4)}$$

Using the obtained values for P_x and the initial partial pressures of CO_2 and H_2 the equilibrium constant can be calculated with equation (V.7-1).

This experiment is repeated for another two values of partial pressures; for example: 100 mm Hg CO_2 + 300 mm Hg H_2 and 300 mm Hg CO_2 + 100 mm Hg H_2.

- *Present in tabular form the obtained results.*

Experimental results will be presented in the following table:

Table V.7-1 Experimental results

No.	Initial temperature	P_{CO_2} (mm Hg)	P_{H_2} (mm Hg)	P_x *(mm Hg)*	K_P	Observations
1		200	200			
2		100	300			
3		300	100			

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OBSERVATIONS

- in order to obtain reproducible results it is necessary that the platinum wire has in each experiment the same temperature. Keeping constant the value of current intensity does not represents a solution because the temperature of the Pt wire depends on the thermal conductibility of gas mixture and that varies during the evolution of chemical process. Therefore, the current must be adjust until resistance of the wire remains constant.
- In the case when the objective of the study is not a simple verify of mass law but the determination of absolute values of K_P, the establishment of wire Pt temperature should be done. This aspect can easily be solved by resistance measurement. There is another calibration method for resistance temperature: the establishment of thermal coefficient of resistance in the range $0 \div 80^0C$ when hydrogen is in the working cell.

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V.8. DISSOCIATION CONSTANT OF A WEAK ACID CONDUCTOMETRIC METHOD

In this experiment we shall be concerned with electrical conduction through aqueous solution. Although water is itself a very poor conductor of electricity, the presence of ionic species in solution increases the conductance considerably. The conductance of such electrolytic solutions depends on the concentrations of the ions and also on the nature of the ions present (through their charges and mobility), and conductance behavior as a function of concentrations is different for strong and weak electrolytes. The weak electrolytes will be studied at a number of dilute concentrations and from the data obtained, the ionization constant can be calculated. By determining the ionization constant at two different temperatures, the enthalpy, the entropy and the Gibbs free energy can be evaluated.

Electrolytic solutions obey Ohm's Law just as metallic conductors do. Thus, the current I passing through a given body is proportional to the potential difference, U; U/I = R, where R is the resistance of the body of solution in ohms. The conductance G is defined as the reciprocal of the resistance:

$$G = 1/R \tag{V.8-1}$$

and is expressed in $ohms^{-1}$ (Siemens). The conductance of a homogeneous body of uniform cross section is proportional to the cross section S and inversely proportional to the length l:

$$R = \rho\frac{l}{S} \Rightarrow \frac{1}{R} = G = \frac{1}{\rho}\cdot\frac{S}{l} = \frac{\gamma\cdot S}{l} \Rightarrow G = \frac{\gamma\cdot S}{l} \tag{V.8-2}$$

$$\gamma = \frac{l}{R\cdot S} = \frac{k}{R} \tag{V.8-3}$$

where γ is the specific conductance in $ohm^{-1}cm^{-1}$. The specific conductance is thus the reciprocal of the resistivity ($\gamma=1/\rho$). The specific conductance of a solution in a cell of arbitrary design and dimensions can be obtained by first determining the cell constant k (the "effective" value l/S) by measuring the resistance of a solution of known specific conductance. A standard solution that can be used for making this calibration is potassium chloride. Once the cell constant has been found, specific conductance can be calculated from the experimental resistance by using equation (V.8-3).

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The specific conductance γ depends on the equivalent concentrations and mobilities of the ions present. For a single electrolyte giving ions A^+ and B^- and having fractional ionization α at a solute concentration c in equivalents per liter, one obtains:

$$\gamma = \frac{\alpha \cdot c \cdot F}{1000}\left(u_{A^+} + u_{B^-}\right) \qquad \text{(V.8-4)}$$

where the u's are the true ionic mobilities and F is the Faraday constant. Thus it is convenient to define a new quantity, the equivalent conductance Λ (molar conductance), by:

$$\Lambda = \frac{1000 \cdot \gamma}{c} \qquad \text{(V.8-5)}$$

Comparing equations (V.8-4) and (V.8-5), we find that:

$$\Lambda = \alpha \cdot F \cdot \left(u_{A^+} + u_{B^-}\right) \qquad \text{(V.8-6)}$$

This equivalent conductance is sometimes described as the actual conductance of that volume of solution that contains one equivalent weight of solute when placed between parallel electrodes 1 cm apart with a uniform electric field between them.

For a strong electrolyte, the fraction ionized is unity at all concentrations, thus Λ is roughly constant, varying to some extent owing to changes in mobilities with concentration but approaching a finite value Λ_0 at infinite dilution.

For a weakly ionized substance, Λ varies much more markedly with concentration because the degree of ionization α varies strongly with concentration. The equivalent conductance, however, must approach a constant value at infinite dilution, Λ_∞, which corresponds to the sum of the limiting ionic conductance:

$$\Lambda_\infty = \lambda_{0,+} + \lambda_{0,-} \qquad \text{(V.8-7)}$$

it is usually impractical to determine this limiting value from extrapolation of Λ values obtained with the weak electrolyte itself, since to obtain an approach to complete ionization the concentration must be made two small for effective measurement of conductance, however, Λ_∞ for a weak electrolyte can be deduced from Λ_0 values obtained for strong electrolytes by the use of equation (V.8-7).

The equivalent conductance, at infinite dilution, Λ_∞, has a constant value, at 25^0C, for succinic acid:

$$\Lambda_\infty = 384\ \Omega^{-1} cm^2 mol^{-1}$$

This value modifies with temperature according to the relation:

$$\left(\Lambda_\infty\right)_t = \left(\Lambda_\infty\right)_{25} \cdot \left[1 + 0.0017 \cdot \left(t - 25\right)\right] \qquad \text{(V.8-8)}$$

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For sufficiently weak electrolytes, the ionic concentration is small and the effect of ion attraction on the mobilities is slight; thus we may assume the mobilities to be independent of concentration and obtain the approximate expression:

$$\alpha \cong \frac{\Lambda}{\Lambda_\infty} \qquad \text{(V.8-9)}$$

Thus it is possible to obtain the degree of ionization of the weak electrolyte at concentration c.

Equilibrium constant for weak electrolyte

Knowing the concentration c of the weak electrolyte, say [HA], and its degree of ionization α, at that concentration, the concentrations of H^+ and A^- ions and of un-ionized HA can be calculated.

$$HA + H_2O \Leftrightarrow H_3O^+ + A^-$$

Then the equilibrium constant in terms of concentrations K_c can be calculated from:

$$K_c = \frac{[H^+]\cdot[A^-]}{[HA]} = \frac{\alpha^2 \cdot c}{1-\alpha} \qquad \text{(V.8-10)}$$

Knowing the values of K_c at two different temperatures: K_1 and K_2 and the connections between equilibrium constant and thermodynamic functions, one can calculate:

$$\Delta G_1^0 = -RT \ln K_1 \qquad \Delta G_2^0 = -RT \ln K_2 \qquad \text{(V.8-11)}$$

$$\Delta H_0 = \frac{R \ln \frac{K_2}{K_1}}{\frac{1}{T_1} - \frac{1}{T_2}} \qquad \text{(V.8-12)}$$

$$\Delta S_1^0 = \frac{\Delta H^0 - \Delta G_1^0}{T_1} \qquad \Delta S_2^0 = \frac{\Delta H^0 - \Delta G_2^0}{T_2} \qquad \text{(V.8-13)}$$

METHOD

Resistance is almost always measured by means of a Wheatstone bridge circuit.

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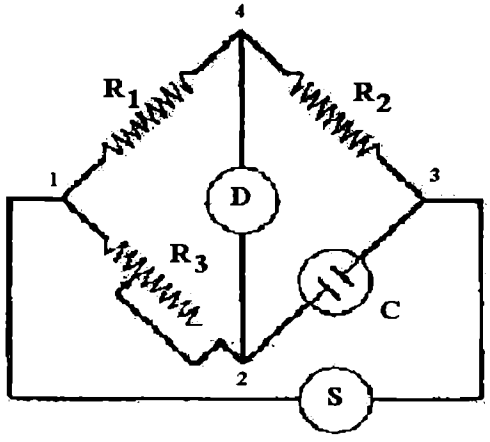

Figure V.8-1 Basic Wheatstone bridge circuit for measurements of resistance

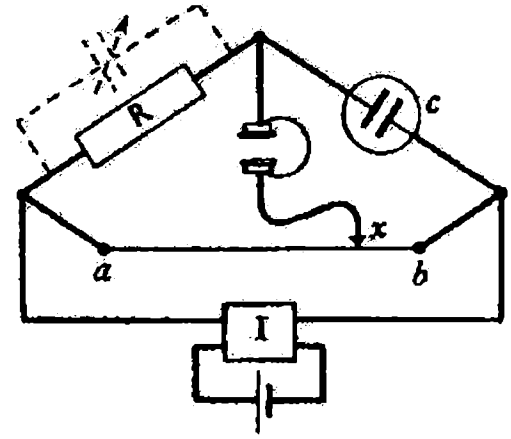

Figure V.8-2 Kohlrausch's conductivity apparatus

S is a source of e.m.f.; **C** is the unknown resistance; $\mathbf{R_1}$, $\mathbf{R_2}$ and $\mathbf{R_3}$ are standard resistances, and **D** is a detector. R_3 is adjusted until the detector indicates no e.m.f. between the points 2 and 4. The bridge is then said to be "balanced", and the resistances must be related to the expression: $R_1/R_2 = R_3/C$ so that $C = R_2R_3/R_1$.

With an electrolytic conductor there are several complications that do not arise with an electronic conductor. The principle one is that the passage of a current causes electrolysis, and a back e.m.f. of "polarization" is set up. This difficulty is overcome by using an alternative current so that whatever electrolysis occurs during the first half-cycle is reversed during the second, and the net electrolysis is negligible. Now it becomes necessary to use for D in place of the usual moving coil galvanometer an instrument capable of detecting small a.c. voltages of the order of 1 millivolt or less. The oldest and still more satisfactory technique for laboratory work is to apply an audio-frequency signal to the bridge and detect the point of balance by disappearance of the sound in sensitive earphones.

The classical early work of Kohlrausch (1898) and other was done with the simple circuit shown in figure V.8-2.

The source of sound is a small induction coil ("buzzer"), I, producing a note of high pitch; R is a resistance box, and the bridge is adjusted by moving the contact x on a straight slide-wire axb until the sound in the earphones is at minimum. At the balance point: $C = Rxb/xa$.

The scheme of our laboratory equipment is presented in figure V.8-3.

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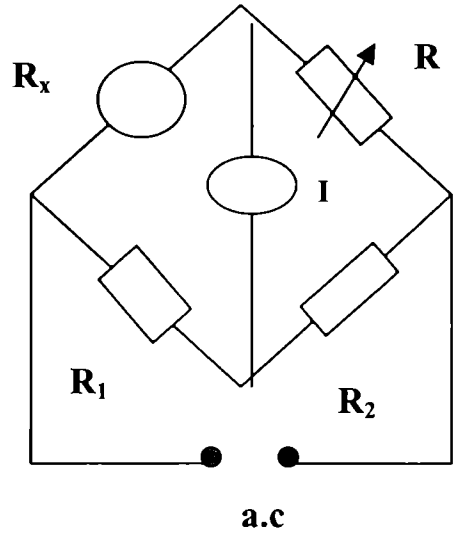

Figure V.8-3 Kohlrausch bridge

I = source of sound
R_1, R_2 = two equal resistance
R = variable resistance (resistance box)
R_x = resistance of a solution which has to be measured
a.c. = alternative curent

At a balance point: $R_x \cdot R_2 = R_1 \cdot R$ (V.8-14)

Because $R_1 = R_2$ results: $R_x = R$ (V.8-15)

The specific conductance of a solution can be measured using a conductivity cell formed by two identical platinum electrodes.

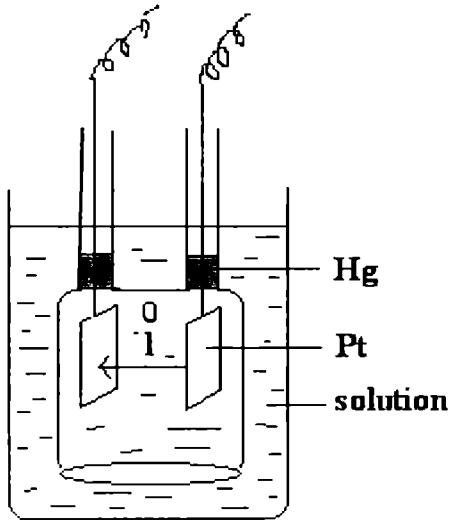

Figure V.8-4 Conductivity cell

The distance between electrodes is **l** and the surface of one electrode is **S**.

The cell constant is the ratio between **l** and **S**.

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$$k_{cel} = \frac{l}{S} = R \cdot \gamma \qquad \text{(V.8-16)}$$

The determination of the value for cell constant will be made by means of conductometric method. It will be measured the resistance of a series of potassium chloride reactions with known values for specific conductance (γ).

APPARATUS AND CHEMICALS

- Kohlrausch bridge with the components presented in figure V.8-3, the detector is a telephone headset, conductivity cell, thermostat (constant temperature bath), 25-ml pipette, two 250-ml beakers, precision resistance box or decade box;
- Distilled water, precisely 0.1 N, 0.01 N, 0.02 N KCl, succinic acid M/32.

EXPERIMENTAL

Setup the circuit as shown in figure V.8-3. Put 0.02 N KCl in a beaker and immerse the conductivity cell. Measure the resistance of this solution at a balance point (adjust the resistance from the resistance box until the sound in the earphones is at minimum. Then read the obtained resistance, which is equal with the resistance of KCl 0.02 N). Repeat the operation with KCl 0.01 N and 0.1 N.

Calculate the cell constant using equation (V.8-16) and the values for specific conductance of KCl from the table V.8-1.

Table V.8-1. Specific conductance for KCl

KCl	0.1 N	0.01 N	0.02 N
γ (Ω^{-1} cm^{-1})	0.012890	0.001412	0.002760

The values of cell constant are an average of the three-recorded values for each solution of KCl.

Rinse very well the beaker and the conductivity cell and then add 40-ml succinic acid M/32. Introduce the conductivity cell and measure the resistance of the solution as described before. Note the obtained value. Then make the first dilution. Extract 20-ml from solution and add 20-ml of distilled water. The resulted concentration is M/64. Measure the resistance of this solution. Repeat the operation

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for another three dilutions (M/128, M/256, M/512). All of these operations were made at room temperature (record the value). The same operations should be made at higher temperature (with at least 10^0C greater) into a thermostat.

CALCULATIONS

- *Determination the constant cell from the equations (V.8-16)*:

$$k_{cell} = R_{KCl} \cdot \gamma_{KCl} \qquad \overline{k}_{cell} = \frac{k_1 + k_2 + k_3}{3}$$

- *Determination the specific conductance for succinic acid using the equation (V.8-16):*

$$\gamma_{HA} = \frac{k_{cell}}{R_{HA}}$$

- *Determination the equivalent (molar) conductivity, Λ, using equation (V.8-5):*

$$\Lambda = \frac{1000 \cdot \gamma}{c}$$

- *Determination the degree of ionization (dissociation), α, using the relation (V.8-9):*

$$\alpha \cong \frac{\Lambda}{\Lambda_\infty} \qquad \text{where } \Lambda_\infty = 384\ \Omega^{-1}cm^2mol^{-1}.$$

- *Determination the equilibrium constant in terms of concentrations using the relation (V.8-10):*

$$K_c = \frac{\alpha^2 \cdot c}{1-\alpha}$$

For each temperature calculates the average value of equilibrium constant: $\overline{K}_1$ and $\overline{K}_2$.

- *Using the values $\overline{K}_1$ and $\overline{K}_2$, calculate the values for the enthalpy, entropy and Gibbs free energy according to the relations (V.8-11), (V.8-12) and (V.8-13):*

$$\Delta G_1^0 = -RT\ln K_1;\ \Delta G_2^0 = -RT\ln K_2;\ \Delta H_0 = \frac{R\ln\frac{K_2}{K_1}}{\frac{1}{T_1}-\frac{1}{T_2}};\ \Delta S_1^0 = \frac{\Delta H^0 - \Delta G_1^0}{T_1};\ \Delta S_2^0 = \frac{\Delta H^0 - \Delta G_2^0}{T_2}$$

- *Present the obtained results in tabular form:*

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Table V.8-2 Experimental data

	T_1					T_2				
c (mol/l)	R_x (Ω)	γ ($\Omega^{-1}cm^{-1}$)	Λ ($\Omega^{-1}cm^2mol^{-1}$)	α	K_1 (mole/l)	R_x (Ω)	γ ($\Omega^{-1}cm^{-1}$)	Λ ($\Omega^{-1}cm^2mol^{-1}$)	α	K_2 (mole/l)
1/32										
1/64										
1/128										
1/256										
1/512										

Table V.8-3 Values for thermodynamics functions

T (K)	K (mole l^{-1})	ΔG (cal mol^{-1})	ΔH (cal mol^{-1})	ΔS (cal $mol^{-1}K^{-1}$)

CONCLUSIONS AND DISCUSSIONS

- explain the variation of equilibrium constant with temperature;
- another acids suitable for this experiment are: benzoic and mandelic acids. Weak dibasic acids such as succinic behave in conductance measurements as monobasic acids since only the first hydrogen is ionized at the concentrations employed.

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V.9. DETERMINATION OF GIBBS FREE ENERGY, ENTROPY AND ENTHALPY FROM THE ELECTROMOTIVE FORCE OF A CELL

The aim of this experiment is to determine the values of Gibbs free energy, entropy and enthalpy for a reaction in a voltaic cell from potential measurements by using of potentiometric method.

The fundamental notions concerning heterogeneous chemical equilibrium between metals and electrolytes are presented in chapter III.e.

METHOD

The emf of a cell is best determined by measurements with a potentiometer, since this method gives a close approach to reversible operation of the cell. The cell potential is opposed by a potential drop across the slide-wire of the potentiometer, and at balance only very small currents are drawn from the cell (depending on the sensitivity of the galvanometer used and the fineness of control possible in adjusting the slide-wire).

APPARATUS AND CHEMICALS

A schematic diagram of potentiometric circuit is presented in the figure 6.2. The bridge is feeded from a 2V battery and the balance point is measured by using of a very sensitive galvanometer (10^{-9} A/unity of scale).

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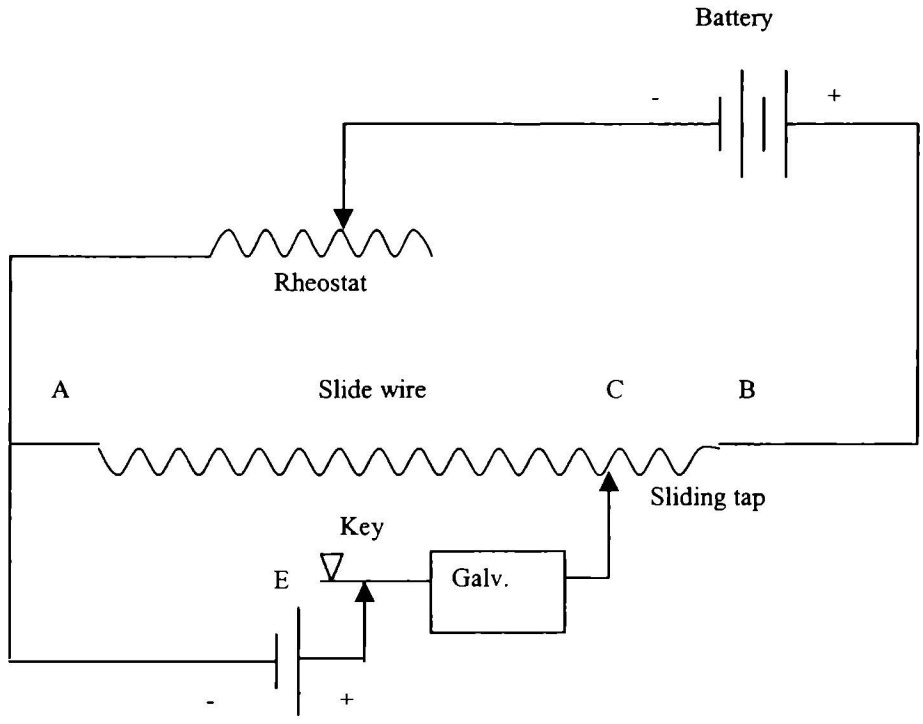

Figure V.9-1 Schematic diagram of a simple slide-wire potentiometer

The investigated voltaic cell has the following construction (figure V.9-2).

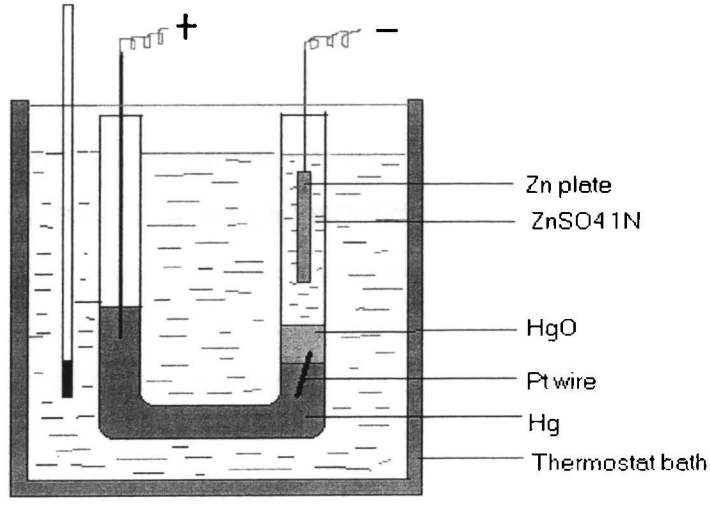

Figure V.9-2 Voltaic cell

$$(+)\ Hg\ /\ HgO\ //\ ZnSO_4\ (1N)\ /\ Zn\ (-)$$

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EXPERIMENTAL

The reactions that take place in the cell are:

- at negative pole:

$$Zn \Leftrightarrow Zn^{2+} + 2e^{-}$$

- at positive pole:

$$HgO + H_2O \Leftrightarrow Hg^{2+} + 2 \cdot HO^{-}$$
$$Zn^{2+} + 2 \cdot HO^{-} \Leftrightarrow ZnO + H_2O$$
$$Hg^{2+} + 2e^{-} \Leftrightarrow Hg$$

The overall process is:

$$Zn + HgO \Leftrightarrow ZnO + Hg$$

The electrochemical cell used as a standard is the Weston cell:

$$(-)Cd(12.5\%Cd \cdot ama\lg am) \cdot CdSO_4 \cdot \frac{8}{3} \cdot H_2O(s), CdSO_4(sat), Hg_2SO_4(s) \cdot Hg(l)(+)$$

which has an emf of 1.0184 absolute volts at 25^0C and a temperature coefficient of $4x10^{-5}$Vdeg^{-1}.

Mount the assembled cell in a thermostat bath. Assemble the potentiometric circuit and connect the cell. Consider the sign of ΔG for the change in state to decide on the proper connection. After the cell has been in the thermostat bath (see figure V.9-2) for at least 10 minutes, measure the emf and repeat this measurement at least three times at 5 minutes intervals to verify that there is no systematic drift in the emf. The potentiometric circuit should be checked against the Weston standard cell immediately before each reading. The emf should be determined as a function of temperature at four or more points in the range from 20 to 50^0C.

CALCULATIONS

- *Determination the experimental values of emf - ε;*
- *The experimental values of emf of the cell will be plotted versus the absolute temperature and from the slope, the thermal coefficient of the efm,* $\left(\partial\varepsilon/\partial T\right)_P$ *will be evaluated (from the best smooth curve through the experimental points);*
- *Using the experimental values of emf, calculate the values of ΔG according to the equation III. 38);*

$$\Delta G = -n \cdot F \cdot \varepsilon$$

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- *By using the value for thermal coefficient of emf, calculate the value for the ΔS, according to the equation (III. 41):*

$$\Delta S = n \cdot F \cdot \left(\frac{\partial \varepsilon}{\partial T}\right)_P$$

- *Calculate the values for ΔH using the equation (III. 42):*

$$\Delta H = \Delta G + T \cdot \Delta S = -n \cdot F \cdot \varepsilon + T \cdot n \cdot F \cdot \left(\frac{\partial \varepsilon}{\partial T}\right)_P = n \cdot F \cdot \left[T \cdot \left(\frac{\partial \varepsilon}{\partial T}\right)_P - \varepsilon\right]$$

- *Present the results in tabular form*

Table V.9-1 Experimental data

T (°C)	**ε** (V)	$\left(\partial\varepsilon/\partial T\right)_P$ **(V/deg)**	**ΔG (kJ/Eg)**	**ΔS (J/Eg.deg)**	**ΔH (kJ/Eg)**

CONCLUSIONS AND DISCUSSIONS

- The value of thermal coefficient for the investigated cell is very small (10^{-3} – 10^{-4} V/deg) and for this reason a constant temperature in the thermostat bath during the period of the measurements is very important;
- Because the entropy of investigated electrochemical reaction is very small, the values for ΔG and ΔH (negative) are very closed.

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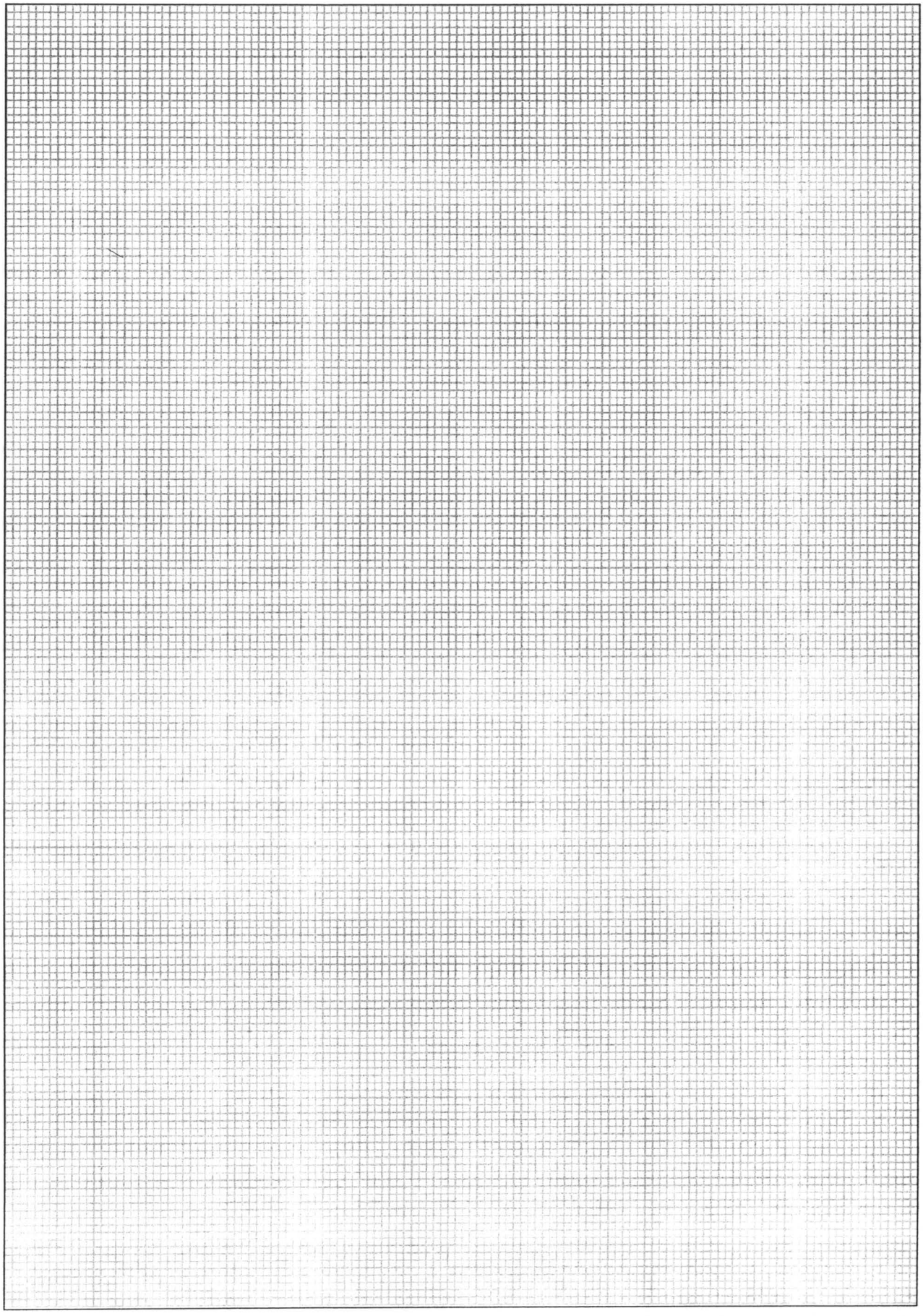

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V.10. DISTRIBUTION OF A SOLUTE BETWEEN TWO NON-MISCIBLE SOLVENTS – THE NERNST DISTRIBUTION LAW

In this experiment, the distribution coefficient of a component between two non-miscible solvents will be calculated.

The equilibrium to be studied is that which arise when acetic acid is distributed between water and benzene.

$$A^{\alpha} \Leftrightarrow A^{\beta} \qquad \text{(V.10-1)}$$

where A is acetic acid, α is water and β represents benzene.

When a substance is "extracted" from aqueous solution by means of a solvent (a common operation in organic chemistry) the extraction is not complete, but the solute distributes itself between the two solvents according to its "solubility" in each. Such solutions cannot both obey Raoult's Law, but as a first approximation, they generally follow Henry's Law, according to which the partial pressure (or activity) of the solute is proportional to its concentration (provided the solutions are very dilute). The proportionality constants are different, however, for the two solvents. It follows, therefore, that at a given temperature, the solute distributes itself in a constant ratio between the two liquids. This ratio, called the *distribution (or partition) coefficient*, is generally approximately independent of the total concentration (**Nernst's Distribution Law**).

Deviations from the law occur when the solute undergoes chemical changes in one of the phases and not in the other. The law is then applicable to the concentration of any particular chemical species in the solutions, although not to the total concentration of the substance.

METHOD

Measurements of the distribution can afford a method of studying such processes as association, dissociation, solvation, hydrolysis, complex formation and "salting-out". Approximate values of the corresponding equilibrium constants may be obtained, but the method is limited quantitatively by the assumption that Henry's Law holds for the species concerned.

No special experimental technique is required.

The equilibrium to be studied is:

$$CH_3COOH^{(water)} \Leftrightarrow CH_3COOH^{(benzene)} \qquad \text{(V.10-2)}$$

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but for the simplification we will use equation (V.10-1) where A is acetic acid, α is water and β represents benzene.

If n moles of acetic acid are involved into the reaction, there is a possibility of their association in benzene. The equilibrium reaction will be:

$$nA^{\alpha} \Leftrightarrow A_n^{\beta} \qquad \text{(V.10-3)}$$

at constant temperature and pressure; the equilibrium constant for the equation (V.10-3) is:

$$K_{T,P} = \frac{\left[A^{\alpha}\right]^n}{\left[A_n^{\beta}\right]} \qquad \text{(V.10-4)}$$

For evaluating the value of distribution constant we have to know the concentrations of acetic acid from the two solvents and the degree of association (n). Determination of the concentrations will be made by means of a normal titration of a weak acid with a strong base (for example sodium hydroxide).

By logarithmation of equation (V.10-4) one can obtain:

$$\ln K_{T,P} = n \ln\left[A^{\alpha}\right] - \ln\left[A_n^{\beta}\right] \quad \Rightarrow \quad \ln\left[A_n^{\beta}\right] = n \ln\left[A^{\alpha}\right] - \ln K_{T,P} \qquad \text{(V.10-5)}$$

By plotting $\ln\left[A_n^{\beta}\right]$ versus $\ln\left[A^{\alpha}\right]$, from the slope of the representation, the degree of association can be obtain.

APPARATUS AND CHEMICALS

- Three separating funnels, three Berzelius beakers, three to six Erlenmeyer flasks, two pipettes (1; 5 ml), one 50-ml burette, rubber bulb for pippeting;
- Distilled water, pure benzene, pure acetic acid, NaOH 0.1N, redox indicator.

EXPERIMENTAL

In three separating funnels, 10 ml from each solvent (water and benzene) should be putted.

In first separating funnel 1-ml acetic acid has to be added.

In the second separating funnel 2-ml and in the last one 3-ml acetic acid has to be added. The three separating funnels containing the solutions should be vigorously shaken for 10 – 15

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minutes and then let the funnels in the stand for few minutes. Then separate the two layers (the lower layer in a beaker and the upper can remain in the separating funnel).

From the aqueous layer take 1-ml, add few drops of redox indicator and titrate with NaOH 0.1N. Note carefully the used volume.

From the benzenic layer take 5-ml, add few drops of redox indicator and titrate with NaOH 0.1N. Record the obtained value of volume. Repeat the above operations for all three aqueous and benzenic layers.

Having the volumes of NaOH, the concentration of acetic acid in the two layers can be calculated. By plotting the logarithm of one concentration $\{\ln[A^{\beta}]\}$ versus the other $\{\ln[A^{\alpha}]\}$, the association degree can be obtain. With this value ($1<n<2$), the distribution constant in each separating funnel can be evaluated.

CALCULATIONS

- *Determination the concentrations of acetic acid in the aqueous layer, using the relation (V.10-7):*

$$V_{NaOH} \times c_{NaOH} = V_{A^{\alpha}} \times c_{A^{\alpha}} \qquad \text{(V.10-6)}$$

$$c_{A^{\alpha}} = \left[A^{\alpha}\right] = \frac{V_{NaOH} \times 0.1}{1} \qquad \text{(V.10-7)}$$

- *Determination the concentrations of acetic acid in the benzenic layer, using the relation (V.10-9):*

$$V_{NaOH} \times c_{NaOH} = V_{A^{\beta}} \times c_{A^{\beta}} \qquad \text{(V.10-8)}$$

$$c_{A^{\beta}} = \left[A^{\beta}\right] = \frac{V_{NaOH} \times 0.1}{5} \qquad \text{(V.10-9)}$$

- *Logarithmation from all values of concentrations;*
- *Plot the $ln[A^{\beta}]$ versus the $ln[A^{\alpha}]$;*
- *Evaluate the slope of the curve which represents the degree of association;*
- *Calculate the distribution constant in each separating funnel using the relation* (V.10-4)

$$K_{T,P} = \frac{\left[A^{\alpha}\right]^{n}}{\left[A_{n}^{\beta}\right]}$$

- *Present in tabular form the experimental data.*

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Table V.10-1 Experimental data

Separating funnel	V_{water} (ml)	$V_{benzene}$ (ml)	$V_{acetic\ acid}$ (ml)	V_{NaOH} (ml)		$[A^{\alpha}]$ (mole/l)	$[A^{\beta}]$ (mole/l)	$\ln[A^{\alpha}]$	$\ln[A^{\beta}]$	$K_{T,P}$
				α	β					
I	10	10	1							
II	10	10	2							
III	10	10	3							

CONCLUSIONS AND DISCUSSIONS

- discuss the obtained values of distribution constant for the three funnels;
- there are other systems suitable for study by the distribution method:
  - *simple partition*: succinic acid between water and ether;
  - *dimmer formation of carboxylic acid*: benzoic acid between water and benzene;
  - *electrolytic dissociation*: monochloracetic acid between water and ether;
  - *hydrolysis of salts*: ammonia between chloroform and copper sulfate solutions;
  - *measurements of activity coefficients*: .hydrochloric acid between water and benzene and salt solutions and benzene.

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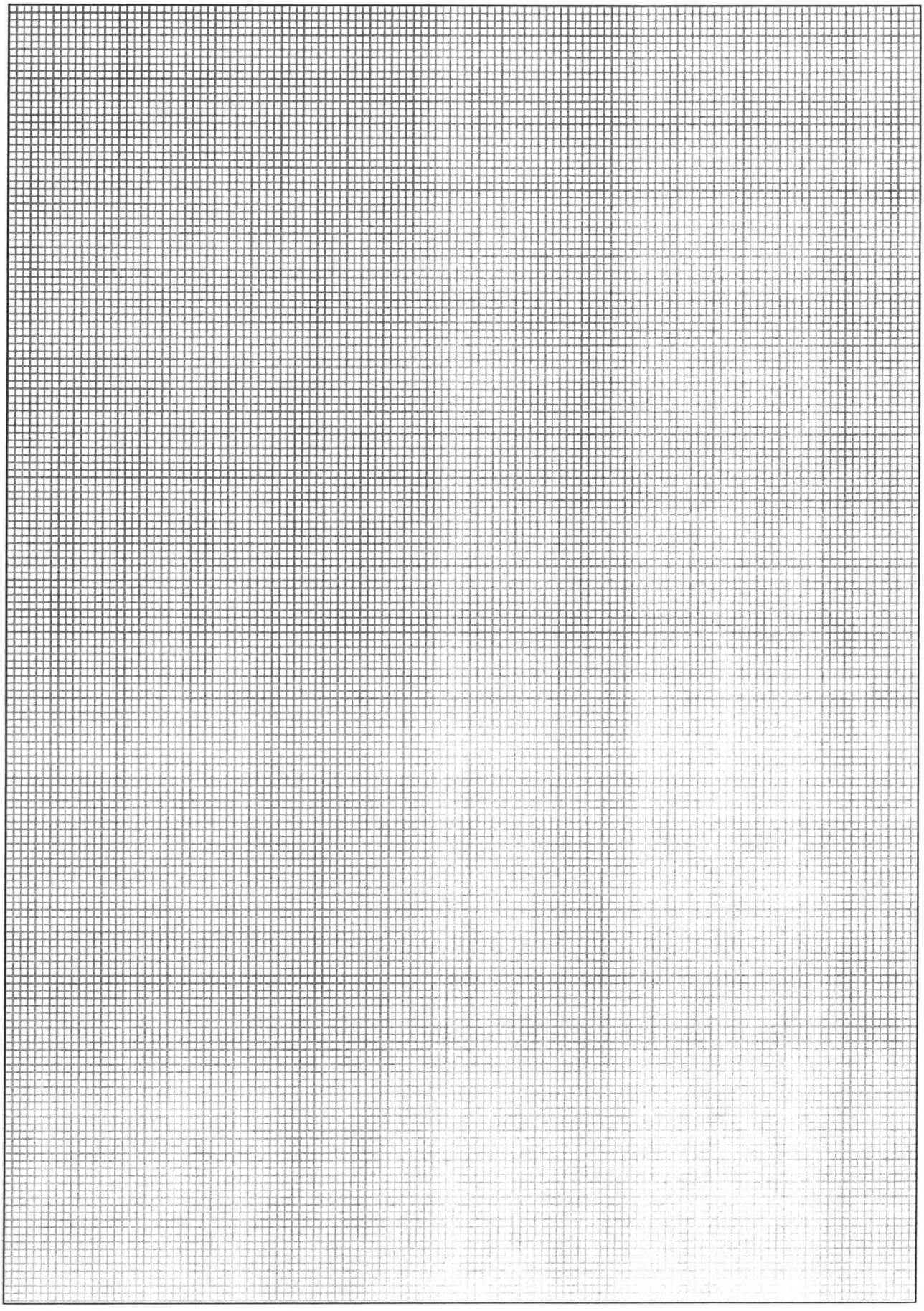

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V.11. THE VAPOR PRESURE OF A LIQUID AS A FUNCTION OF TEMPERATURE

When a pure liquid is placed in an evacuated bulb, molecules will leave the liquid phase and enter the gas phase until the pressure of the vapor in the bulb reaches a definite value, which is determined by the nature of the liquid and its temperature. This pressure is called the vapor pressure of a liquid at a given temperature. The equilibrium vapor pressure is independent of the quantity of liquid and vapor present as long as both phases exist in equilibrium with each other at the specified temperature. As the temperature is increased, the vapor pressure also increases up to the critical point, at which the two-phase system becomes a homogeneous, one-phase fluid.

If the pressure above the liquid is maintained at a fixed value (say by admitting air to the bulb containing the liquid), then the liquid may be heated up to a temperature at which the vapor pressure is equal to the external pressure. At this point, vaporization will occur by the formation of bubbles in the interior of the liquid as well as at the surface; this is the boiling point of the liquid at the specified external pressure. Clearly the temperature of the boiling point is a function of external pressure; in fact, the variation of the boiling point with external pressure is seen to be identical with the variation of the vapor pressure with temperature.

In this experiment the variation of vapor pressure with temperature will be measured and used to determine the molar heat of vaporization.

This experimental work is an application of liquid-vapor equilibrium in monocomponent system. The theory is detailed presented in chapter IV. b.

The equilibrium between a pure liquid and its vapor can be written:

$C^l \Leftrightarrow C^g$ (P, T)

For the case of vapor-liquid equilibria in the range of vapor pressures less than 1 atm, one may assume that the molar volume of the liquid V^l is negligible in comparison with that of the gas V^g, so that $\Delta V^g = V^g - V^l \cong V^g$. This assumption is very good in the low-pressure region, since V^l is usually only a few tenth of a percent of. V^g. Thus we obtain:

$$\frac{dP}{dT} = \frac{\Delta^v H}{T \cdot V^g} \qquad \text{(V.11-1)}$$

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Since $p \cdot V^g = R \cdot T$ and $d \ln P = \frac{dP}{P}$, we can rewrite equation (V.11-1) in the form:

$$\frac{d \ln P}{dT} = \frac{\Delta^v H}{RT^2} \qquad \text{(IV.13)}$$

Assuming that the heat of vaporization is constant and independent of temperature, integration of equation (IV.13) gives:

$$\ln P = -\frac{\Delta^v H}{R \cdot T} + const. \qquad \text{or} \qquad \log P = -\frac{\Delta^v H}{2.303 \cdot R \cdot T} + const. \qquad \text{(V.11-2)}$$

If the vapor pressure of a liquid is determined at a series of temperatures, a plot of ln P against 1/T should give a straight line. $\Delta^v H$ may be determined from the slope of this graph.

METHOD

There are several experimental methods of measuring the vapor pressure as a function of temperature. In the *gas-saturation method* a known volume of an inert gas is bubbled slowly through the liquid, which is kept at constant temperature in a thermostat. The vapor pressure is calculated from a determination of the amount of vapor contained in the outcoming gas or from the loss in weigh of the liquid. A common *static method* makes use of a *isoteniscope*, a bulb with a short U tube attached. The liquid is placed in a bulb, and some liquid is placed in the U tube. When the liquid is boiled under reduced pressure, all air is swept out of the bulb. The isoteniscope is then placed in a thermostat. At a given temperature the external pressure is adjusted so that both arms of the U tube are at the same height. At this setting, the external pressure, which is equal to the pressure of the vapor in the iosteniscope, is measure with a mercury manometer. A common *dynamic method* is one in which the variation of the boiling point with external applied pressure is measured. The total pressure above the liquid can be varied and maintained at a given value by use a large-volume ballast bulb; this pressure is then measured with a mercury manometer. The liquid to be studied is heated until boiling occurs, and the temperature of the refluxing vapor is measured in order to avoid any effects of superheating. In this experiment the dynamic method will be used.

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APPARATUS AND CHEMICALS

- Ballast bulb, closed-tube manometer, double-neck distillation flask (Claissen flask), a Celsius thermometer to cover the desired range, reflux condenser, electric bath, rubber tubing for circulating water through condenser, rubber pressure tubing;
- Liquid, such as distilled water, n-heptane, cyclohexane or 2-butanone.

EXPERIMENTAL

The apparatus is assembled as shown in figure V.11-1.

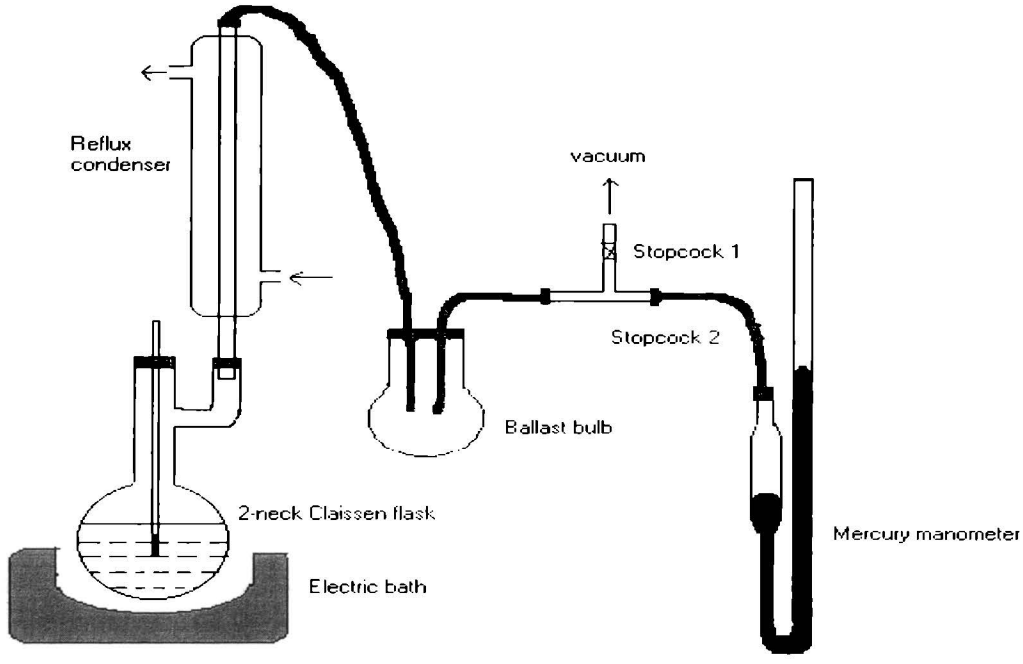

Figure V.11-1 Experimental device

A Claissen distilling flask is used in this experiment by closing off the side arm with a rubber. The reflux condenser and the manometer are connected to the ballast bulb by using rubber tubing. The flask is filled about one-third with the liquid to be studied (water). A few marble-boiling chips should be added to reduce "bumping". Heating is accomplished by using of an electric heating bath placed directly below the flask.

The use of the manometer must be made with a greatest care in order to prevent liquid condensation in it. To make a reading, adjust the heating so as to attain steady boiling of the liquid, but

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avoid heating to strongly. When conditions appear to be steady, open stopcock 2 carefully and watch the manometer. When manometer and thermometer appear to be as steady as they can be maintained read them as nearly simultaneously as possible.

To change the pressure in the system between measurements, first remove the heater, then check to make sure that the stopcock 2 is closed. After short time admit some air by opening stopcock 1 for a few seconds. Then open stopcock 2 carefully to measure the pressure on the manometer. The increase of pressure must be of about 20 – 30 mm Hg. Repeat as often as necessary to attain the desired pressure (minimum ten experimental values). Close the stopcock 2 and restore the electric bath to its position under the flask.

CALCULATIONS

- *Determine the values of vapor pressures of water at different temperature;*
- *Calculate the lnP and 1/T then plot the obtained values for lnP versus 1/T;*
- *Determine the slope of the graph and calculate the* $\Delta^v H$ using the equation (V.11-2):

$$\Delta^v H = -R \cdot tg\alpha \qquad \text{(V.11-3)}$$

- *Present in tabular form the obtained results.*

Table V.11-1 Experimental data

t (^{0}C)	T (K)	1/T (K^{-1})	p (mm Hg)	ln p	tgα (K)	$\Delta^v H$ (cal/mole

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CONCLUSIONS AND DISCUSSIONS

- Using the equation (V.11-2) we can estimate the variation in $\Delta^{v}H$ over a range of studied temperature. The obtained results can indicate whether $\Delta^{v}H$ should increase or decrease with increasing temperature;
- By using of different pairs of experimental values situated on different points on the plot lnP versus 1/T we can appreciate the uncertainty in the value of $\Delta^{v}H$. The estimation of $\Delta^{v}H$ from the slope leads to an average value;
- By comparison of the average value of $\Delta^{v}H$ with the above-mentioned values, we can appreciate possible systematic sources of errors.

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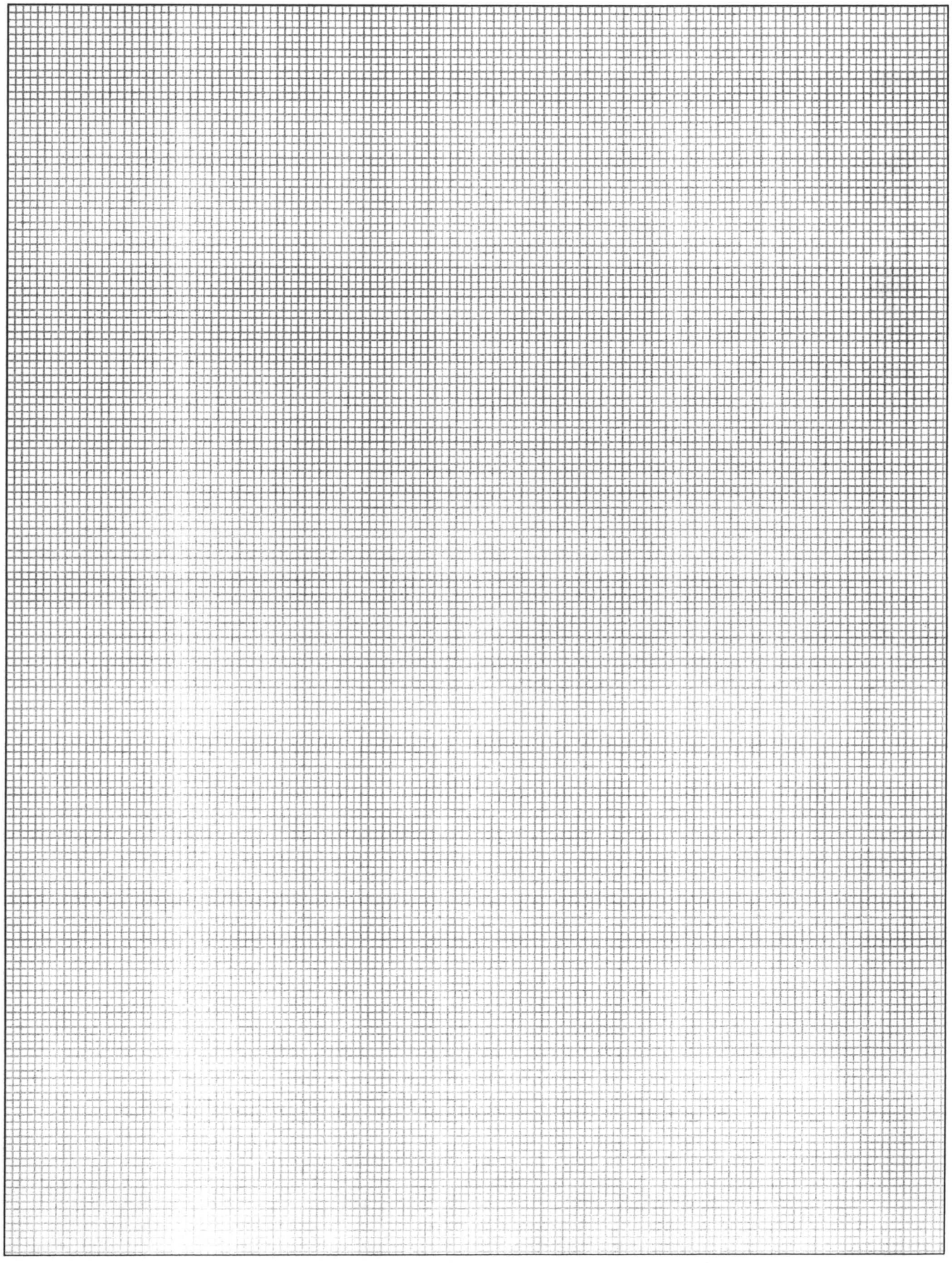

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V.12. THE VAPOR - LIQUID EQUILIBRIUM FOR AN AZEOTROPIC MIXTURE

In the chapter IV. b we presented the theoretical basis of formation of azeotropic mixture. The aim of this experimental work is to show a method for obtaining data that allow drawing a liquid – vapor diagram.

METHOD

In the most chemical processes, the quality of obtained products is conditioned from the purity of chemical reagents. The theoretical and experimental studies indicate that techniques are dealing with the problem of obtaining of some high purity compounds from multicomponent mixtures. Azeotropic mixtures represent major impediments in achievement of this desiderate.

The experimental method that will be presented is based on liquid – vapor equilibrium principle with phase re-circulation. The use of refractometric method allows an exactly analyze of the composition of liquid and vapor phases.

APPARATUS AND CHEMICALS

The mains parts of the experimental device are:

- Equilibrium cell;
- Thermostat;
- Abbe refractometer.

As chemical reagents will be used bidistilled water and pure n-propanol.

EXPERIMENTAL

The experimental device is presented in figure V.12-1

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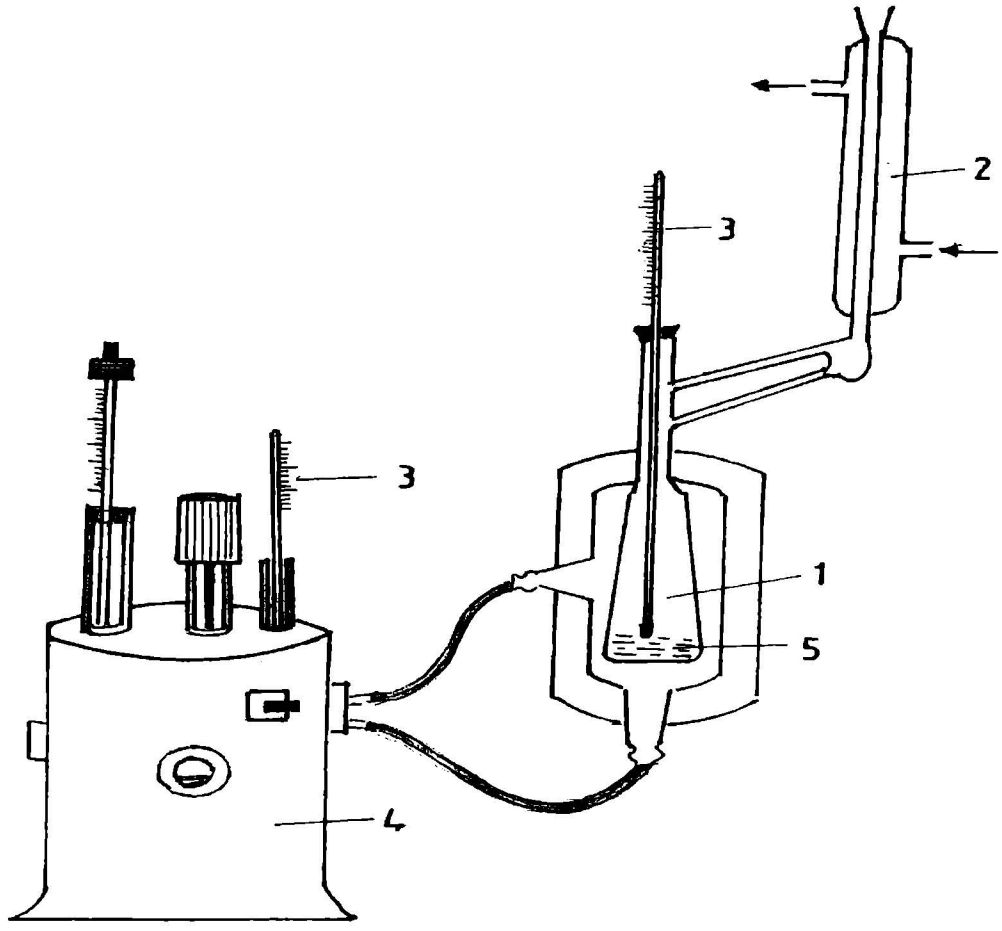

Figure V.12-1 Experimental device

The working cell (1) (figure V.12-1) made from Pyrex glass is protected against the environmental by 2 glass mantles soldered at this. The first mantle is evacuated ($\approx 10^{-5}$ mm Hg) and the second is connected to a thermostat (4) that allows to establish temperature control with 0.02^0C precision (3).

The working procedure contains several distinct stages:

- 12 mixtures water – n-propanol mixture (5) with composition between 0.1 ÷ 1 molar fractions are prepared. For each composition, the refraction index is very exact measured. Finally, with so obtained values, the plot refraction index versus composition will be drawn. The data for graphical representation of the calibration curve are presented in the following table:

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Table V.12-1 Experimental data for calibration curve (water – n-propanol system)

Water (1) [cm^3]	n-propanol (2) [cm^3]	n_1	n_2	$n_1 + n_2$	x_2	n_D^{20}
5	5	0.2778	0.0669	0.3447	0.1941	1.3660
5	4	0.2778	0.0535	0.3313	0.1615	1.3625
5	3	0.2778	0.0401	0.3179	0.1261	1.3575
5	2	0.2778	0.0767	0.3045	0.0877	1.3540
5	1	0.2778	0.0134	0.2912	0.0461	1.3460
4	5	0.2222	0.0669	0.2891	0.2314	1.3685
3	5	0.1667	0.0669	0.2336	0.2864	1.3720
2	5	0.1111	0.0669	0.1780	0.3758	1.3760
1	5	0.0556	0.0669	0.1225	0.5707	1.3810
0.1	5	0.0056	0.0669	0.0725	0.9228	1.3850
0.5	5	0.0278	0.0669	0.0947	0.7067	1.3838
0.75	5	0.0417	0.0669	0.0836	0.5016	1.3823
pure	0	pure	0	-	-	1.3330
0	pure	0	pure	-	-	1.3855

- the thermostat (4) will be start and the temperature will be rise slowly until the liquid (5) starts to boil, and when the dynamic equilibrium is establish (a constant reflux at refrigerant, 2), temperature is recorded (3);
- with the aid of a microsyringe, samples from condense phase (6) are taken and then are refractometric analyzed;
- this operation is repeated for all 12 mixtures.

CALCULATIONS

- *Using the obtained data, the liquid – vapor equilibrium diagram is plotted. Values of composition and temperature for azeotropic mixture is noted*;

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- *The data so obtained can be used to calculate the activity coefficients of solvent and solute in connection with an appropriate model.*
- *Present in tabular form the obtained results.*

Table V.12-1 Experimental data for water – n-propanol system

n_D^{20}	1	2	3	4	5	6	7	8	9	10	11	12
x_2^l												
x_2^g												

CONCLUSIONS AND DISCUSSIONS

- From the examination of so obtained diagram, the first Gibbs-Konovalov theorem is confirmed. According with this, the saturated vapor phase, in connection with the solution, is richer in the component that added to solution increases the total vapor pressure;
- At constant pressure, according to phase rule (F = 1), establishing the temperature or the composition should be sufficient for defining the liquid-vapor equilibrium in azeotropic mixtures (constant boiling temperature at azeotropic composition).

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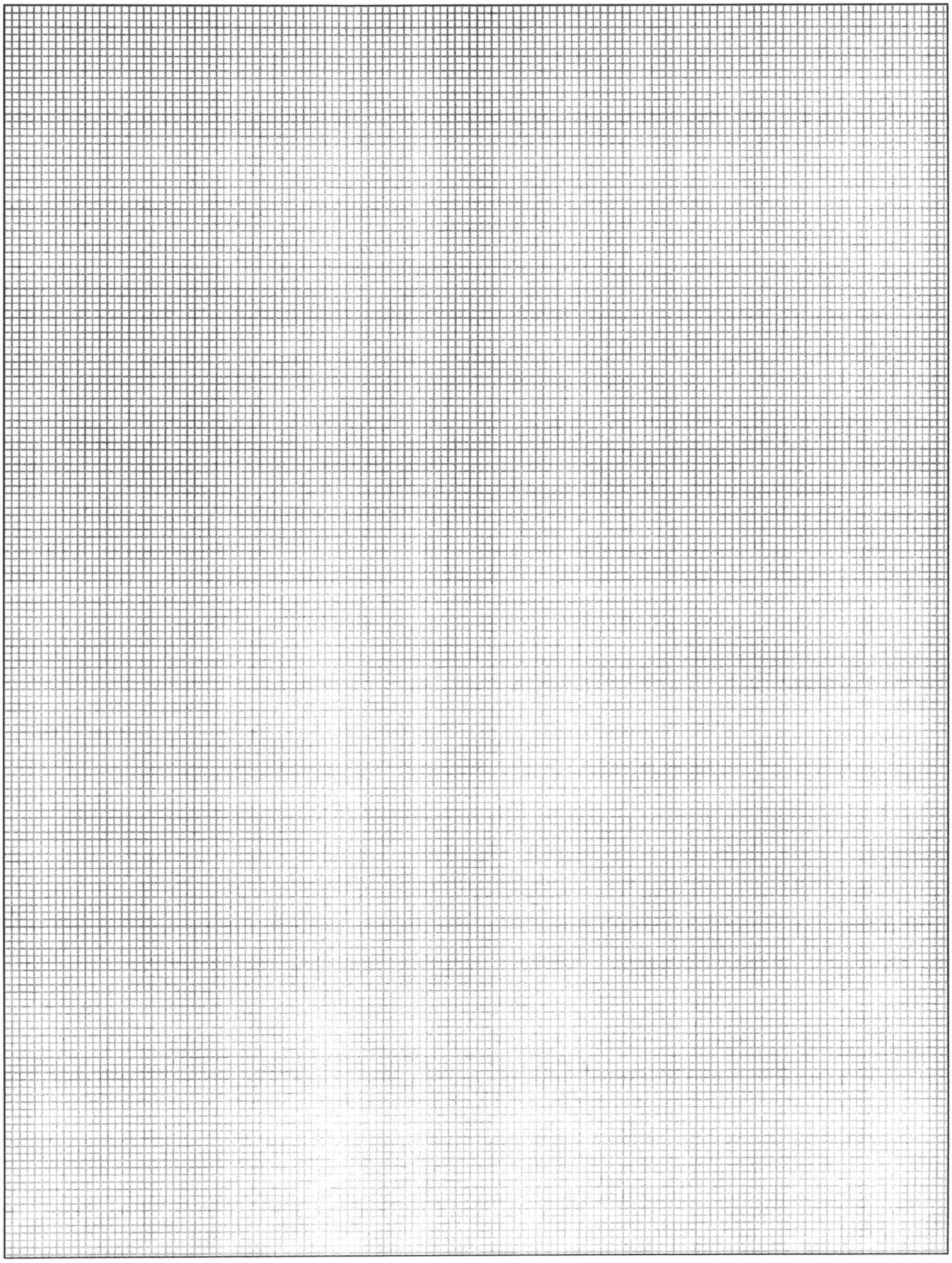

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V.13. SOLUBILITY OF GASES IN LIQUIDS

Numerous examples in nature illustrate the ability of liquids to dissolve gases; indeed, human life would not be possible if blood could not dissolve oxygen, nor could marine life exist if oxygen did not dissolve in water. Gas mixtures can be separated by absorption because different gases dissolve in a liquid in different amounts and therefore most gaseous mixture can be separated by contact with a suitable solvent, which dissolves one gaseous component more than another.

The solubility of gas in a liquid is determined by the equations of phase equilibrium (see chapter IV.c).

In this experiment we shall determine the solubility of CO_2 in N–methyl-pyrolidone at 25^0C and pressures up to 50 bar.

METHOD

The schematic diagram of the equipment is presented in figure V.13-1. The gas supply system consists of a compressed gas bottle (1), a steel cylinder (2) for eliminating water traces using molecular sieves, an autoclave (3) and a fine handling of gas supply the equilibrium cell (7). The equilibrium cell is made of stainless steel with an inner volume of about 100 ml suspended with two metal pillars on a plastic plate tightly fixed on a thermostat. The equilibrium cell, filled up with solvent, is rocked and stirred by means of an electromechanical device placed in the thermostat bath (6) (figure V.13-2). An intensive mixing of the two phases is thus achieved and phase equilibrium can therefore be attained in a few hours. Three capillary tubes made of stainless steel (0.2 mm inner diameter) passing through the equilibrium cell cover serve as follows: the first for direct gas supply in the liquid phase, the second one for sampling of liquid saturated with the gas to be analyzed and the third one to eliminate the gas phase and to evacuate the equilibrium cell. As thermostating liquid ethylene glycol – water mixture was used allowing measurements for a wide range of temperatures. The sampling and analyzing system contains a condenser (8), an ampoule for samples (9), a thermostated reservoir (10), a mercury manometer (11) and a precision cathetometer. The role of the condenser is to condense the solvent vapors from the sample for very volatile solvents. The thermostated vessel (10) with an inner volume of 2000 ml is an expansion burette with a manometer (11) and a cathetometer (precision: ± 0.01 mm).

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The pressure measurements system works in two steps: the first one for the gas supply is controlled by a manometer with Bourdon tube (precision class 0.6) and the second one for phase equilibrium achievement using a pressure gauge (5) with rotative piston and weights (precision class 0.5). In order to avoid the condensation of solvent vapors in the pressure measuring system, a differential pressure manometer (4) was used.

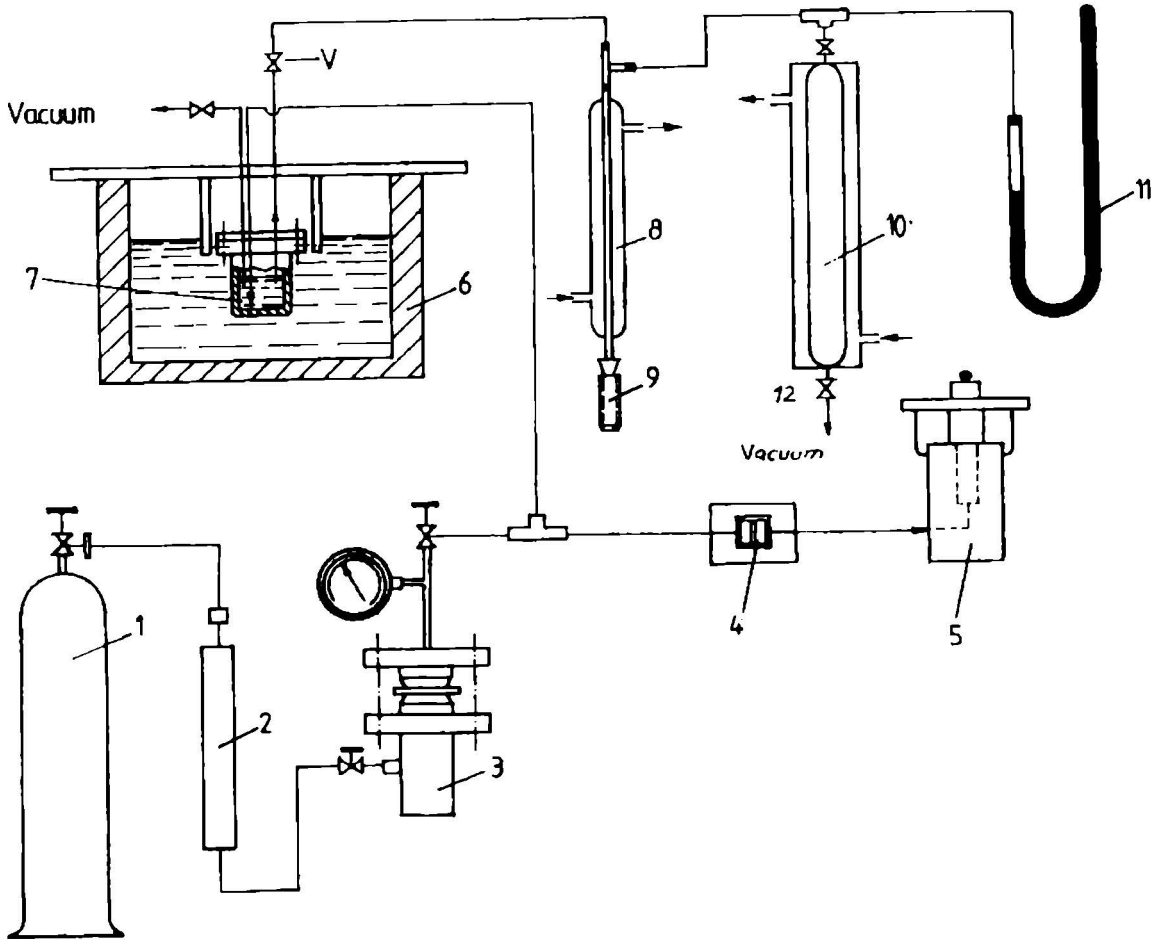

Figure V.13-1. Schematic diagram of the experimental equipment

APPARATUS AND CHEMICALS

The equipment, schematically presented in figure V.13-1, contains the following components:

- Controlled supply system for purified gas;
- Equilibrium gas – liquid cell provided with thermostating system;

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- Sampling and analysis system for measuring the amount of dissolved gas;
- Pressure measuring system;
- Cathetometer;
- CO_2 and N–methyl-pyrolidone.

EXPERIMENTAL

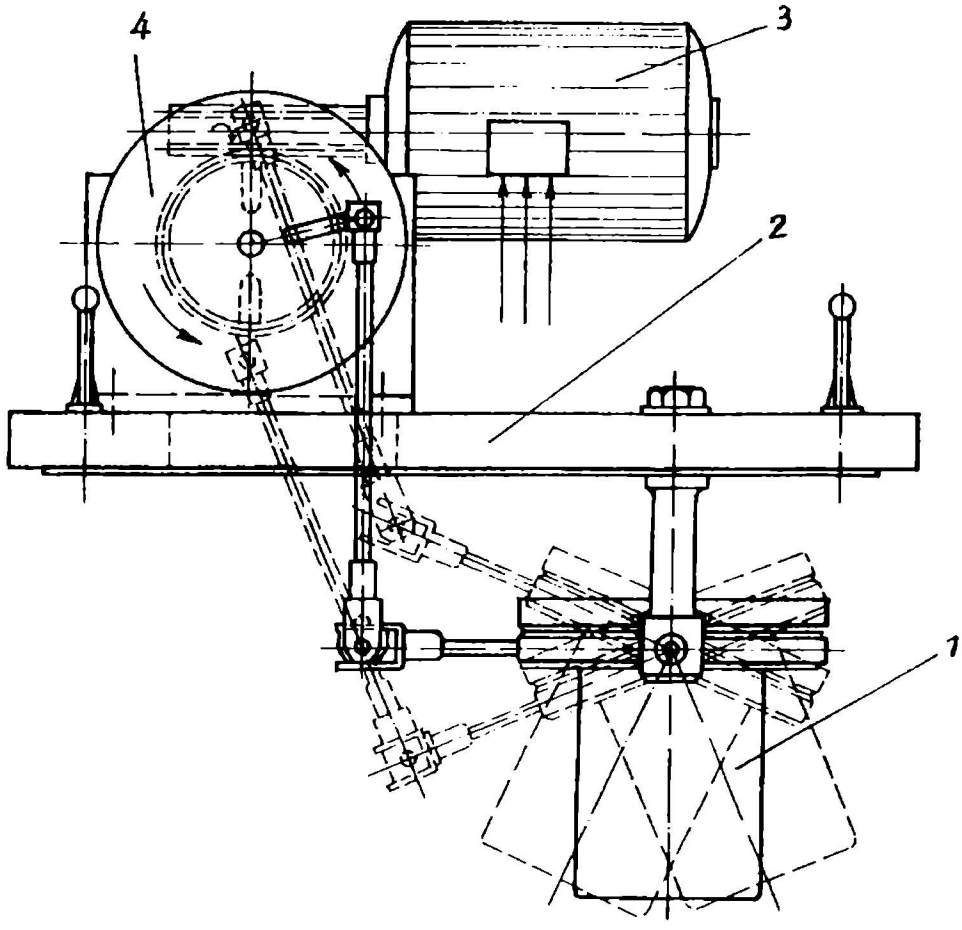

Figure V.13-2. The equilibrium cell with the electromechanical device: 1, equilibrium cell; 2, plastic plate; 3, electric motor; 4, mechanical device

The equilibrium cell is first washed and then dried. It is filled with about 50 ml of solvent, the cover is closed, attached to the stirrer and introduced into a Lauda Thermostat (6) (model K4R) provided with an electronic system and Pt thermometer (accuracy of ± 0.02 K). After vacuum is ensured in the equilibrium cell and the thermostat is set at the desire temperature, gas is slowly supplied

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up to a pressure value higher than that requested for the phase equilibrium. The equilibrium is attained under an energetic stirring within a few hours. After sampling system has been evacuated, the valve (V) is carefully opened. A sample of about 1 ml of solvent is thus collected in the ampoule (9). The dissolved gas is then desorbed and the pressure produced in this way is read by means of the cathetometer. In order to ensure that all the studied gas been desorbed from the sample drawn from the equilibrium cell, the solvent has been tested. After the gas desorption no refractive, spectral and density modification have observed in comparison with the initial properties. The volume, pressure, temperature and mole number of the desorbed gas can be correlated using a simple equation of state taking into account the low values of the pressure. We have used the virial equation of state containing only the second virial coefficient. After pressure reading, the valve (12) is opened and air at atmospheric pressure is introduced. The ampoule (9) is then removed and weighed. The volume of solvent is easily estimated (max. estimated error: $\pm 10^{-3}$ cm^3) knowing the solvent density and the mass of ampoule. The volume of the desorbed gas, V_g, is determined (max. estimated error: $\pm 10^{-2}$ cm^3) by means of the equation:

$$V_g = V_8 + V_9 + V_{10} + V_{11} - V_s + SP/2 \qquad \text{(V.13-1)}$$

where V_8, V_9, V_{10}, V_{11} and V_s are respectively, the volumes of the condenser, ampoule, expansion burette, manometer left branch (until vacuum level) and sampling solvent. S is the manometer section area and P is the desorbed gas pressure.

CALCULATIONS

- *Knowing the mass of empty ampoule and weighing the ampoule filled with the solvent from which the CO_2 was desorbed, one can obtain the mass of N–methyl-pyrolidone (m_s);*
- *From experimental data concerning the desorbed gas: the volume (see equation V.13-1), pressure and temperature one can calculate the mole numbers of CO_2 (n_2^l) by using of the equation of ideal gas:*

$$p \cdot V_g = n_2^l \cdot R \cdot T$$

- *By using of the mole number of N–methyl-pyrolidone, $n_1^l = {m_s}/{M_s}$ and the mole number of CO_2 (n_2^l), the solubility of carbon dioxide, as mole fraction (x_2^l) can be calculated:*

$$x_2^l = \frac{n_2^l}{n_1^l + n_2^l}$$

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CONCLUSIONS AND DISCUSSIONS

- Apart from the solubility of solids and liquids, the experimental study of solubility of gases in liquids is more difficult. The equilibrium state can be obtained after some hours only with the help of electromechanical system that allows a vigorous stirring of the two phases;
- The equilibrium state is attained when, for a long time, no modification in temperature and pressure of the system is observed;
- The using of ideal gas equation of state to correlate the mole number of desorbed gas is justified by the low value of the pressure.

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V.14. BINARY SOLID – LIQUID PHASE DIAGRAM WITH EUTECTIC

Solid – liquid equilibria differ from liquid – vapor equilibria in being essentially independent of pressure changes of order of few atmospheres. This is a consequence of the Clapeyron equation owing to the small molar volume change associated with fusion. Accordingly we shall be concerned only with temperature – composition diagram at atmospheric pressure.

From the many systems that are suitable for this study, the system p-nitrophenol – naphthalene has been selected for this experiment because of the simplicity of their phase diagram and the convenience of its temperature range.

For a binary system with miscible components in the liquid phase and non-miscible in the solid phase, the phase equilibria can be written:

$$(C_1 + C_2)^l \Leftrightarrow C_1^s$$
$$(C_1 + C_2)^l \Leftrightarrow C_2^s$$

The equations that characterized liquid-solid equilibrium were presented in chapter IV.d.

METHOD

The relations of cooling curves to phase diagram (as illustrated in figure IV.2 in chapter IV.d) forms the basis of thermal analysis, an important technique for determining phase diagram.

The interpretation of such curves is often subject to experimental difficulties. A frequent difficulty is supercooling, which tends to obscure breaks or make them difficult to distinguish from short arrest. When the initial composition is far from the eutectic, the thermal arrest at the eutectic temperature is often hard to observe, since the amount of liquid is small relative to the amount of solid already formed and stirring becomes very difficult. When solid solubility exists, it is often very difficult to obtain the true "solidus" curve from cooling curves. For the system p-nitro-phenol – naphthalene, a reasonable number of cooling curves can be easily obtained using a thermocouple to measure the temperature. The thermocouple can be attached to an electronic recorder (as a potentiometer) and thus the cooling curves and the arrest and breaks can be easily observed.

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APPARATUS AND CHEMICALS

- Nine test tubes (20 ml capacity) with wire stirrers, copper-constantan thermocouples, potentiometer;
- P-nitro-phenol, naphthalene

EXPERIMENTAL

The material to be used should be of reagent grade. The mixtures having a composition as indicated in the table V.14-1 are introduced in nine test tubes with about 20 ml capacity. The test tubes have a form as indicated in the figure V.14-1.

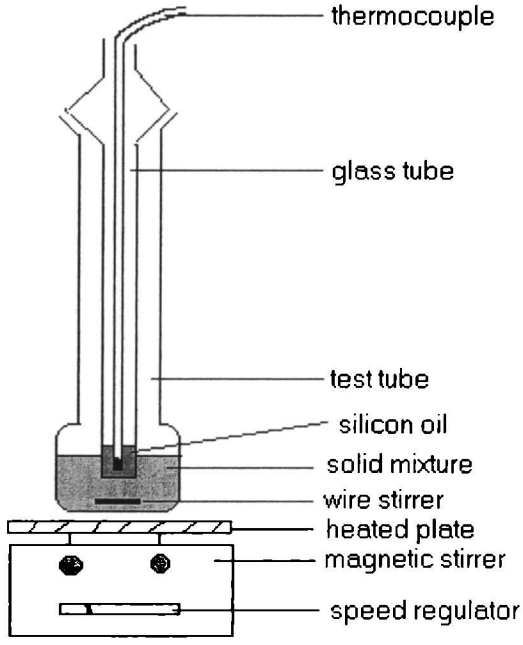

Figure V.14-1. Experimental device

The thermocouple is mounted in a closed glass tube (8 mm in diameter) and the junction is immersed in silicon oil at the bottom of the glass tube. In order to obtain a uniform temperature of the melting mixture, at the bottom of the test tube is introduced a wire stirrer. With the help of the heated

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plate of the magnetic stirrer, the cooling rate can be regulated and thus we can prevent a supercooling of the mixture.

In order to obtain a cooling curve, the test tube containing the mixture is heated in a silicon oil bath until the solid is completely melted. Then the tube is placed on the heated plate of the magnetic stirrer. Stir continuously and follow the running of the temperature on the recorder. After each run determines break and arrest temperatures. From the results of runs 1 through 9 draw the liquidus curves and determine the eutectic composition.

CALCULATIONS

- *Plot the break and arrest temperatures against the overall composition X_2;*
- *Draw the eutectic line at the liquidus curves;*
- *Label all fields to show the phases present;*
- *From the limiting slopes of the liquidus curves estimate the heats of fusion of* C_1^s and C_2^s, *assuming that there is no appreciable solid solubility*

Table V.14-1 Suggested compositions for thermal analysis ($x_1 = x_{\text{p-nitro-phenol}}$, $x_2 = x_{\text{naphthalene}}$). Total mass is 10 grams.

x_1	x_2	m_1 (g)	m_2 (g)
0.1	0.9	1.07668	8.92331
0.2	0.8	2.13517	7.86482
0.3	0.7	3.17593	6.82406
0.4	0.6	4.19939	5.80060
0.5	0.5	5.20599	4.79400
0.6	0.4	6.19613	3.80386
0.7	0.3	7.17022	2.82977
0.8	0.2	8.12865	1.87134
0.9	0.1	9.07179	0.92820

$t_1^0 = 113^0$ C (386.16 K), $t_2^0 = 80.5^0$ C (353.66 K)

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CONCLUSIONS AND DISCUSSIONS

- A method sometimes is used for obtaining the liquidus curve in a system of sufficient optical transparency is the determination of the "clear point" (the temperature at which the last solid disappears on warming) and of the "cloud point" (the temperature at which the first solid appears on cooling) for each of a number of compositions.
- Other system that can be studied is diphenylamine – naphthalene.

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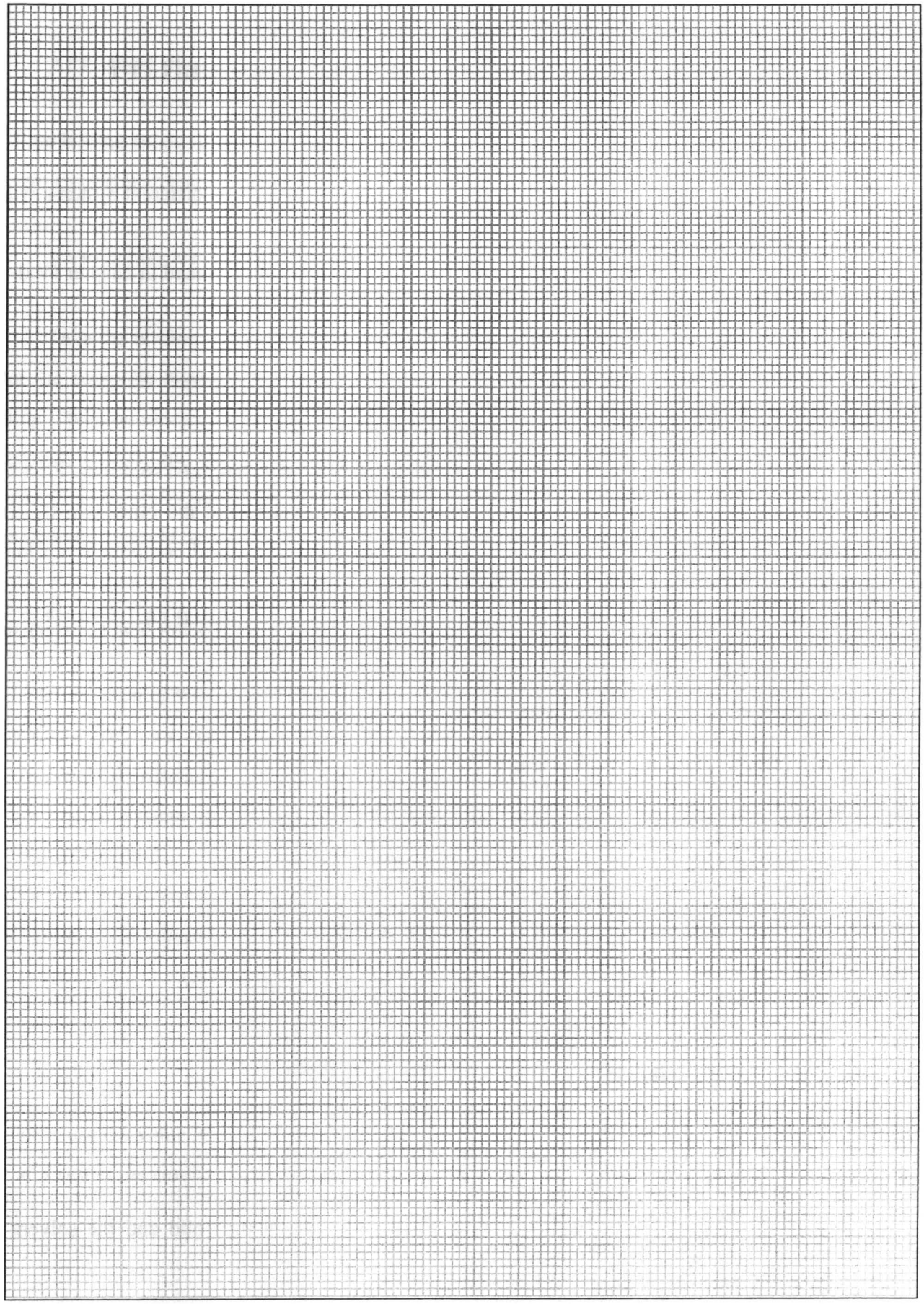

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V.15. TEMPERATURE DEPENDENCE OF SOLUBILITY

In this experiment, the values of integral heats of dissolution for two different systems will be evaluated.

The way in which solubility varies with temperature was detailed presented in chapter IV.d.

METHOD

No special experimental technique is required.

For this experiment we need five boiling – tubes filled with supersaturated solutions. First three boiling – tubes (1, 2, 3) contain an inorganic system: KNO_3 in water, and the other two (I, II) an organic system: naphthalene in toluene. The molar fractions of the dissolved component are known (see table V.15-1).

The boiling – tubes have an interior tube filled with paraffin oil (for a better heat transfer) and it can hold a thermometer.

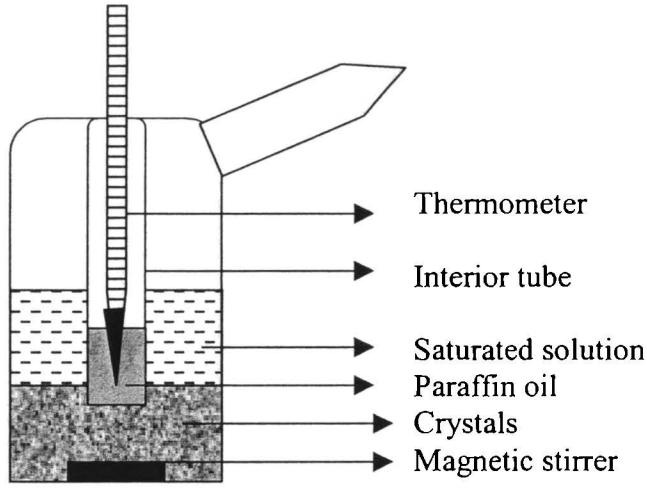

Figure V.15-1 Boiling - tube

Also, the boiling – tube contains a magnetic stirrer by which the solid and the solvent are vigorously stirred.

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APPARATUS AND CHEMICALS

- Five boiling tubes filled with the working systems (according to table V.15-1); two thermometers, two electrical stirrers, one heating bath (with water).

EXPERIMENTAL

Take the boiling – tubes and introduce them into a heating bath. Allow the crystals to dissolve. After the complete dissolution, take off one boiling – tube and allow it to cool. For cooling, put the boiling – tube on electrical stirrer and introduce a thermometer inside of interior tube. The solution are vigorously stirred (and the temperature will be recorded every 30 seconds) until the crystals start to appear. Note carefully the value of the temperature at which crystals appear and write it in the table 1. This operation should be repeated for all boiling – tubes.

CALCULATIONS

- *Determination of the temperature for all 5 boiling – tubes:*
  $t(^0C) \rightarrow T(K) \rightarrow 1/T(K^{-1})$
- *Graphical representation of* lgx_2^{sat} *versus (1/T) for both systems.*
  For organic system will be consider the third point at $x_2 = 1$ and $t = 80.2^0C$ (the fusion temperature for naphthalene).
- *For both curves (straight lines) evaluate the values of the slopes (tgα);*
- *Determine the values of enthalpy of dissolution at saturation from the equation (IV.34) in which:*

$$\ln x_2^{sat}(T) = -\frac{\Delta H_{dis}^{sat}}{R \cdot T} + const. \qquad \text{(IV.34)}$$

in which: $tg\alpha = -\frac{\Delta H_{dis}^{sat}}{R} \Rightarrow \Delta H_{dis}^{sat} = -R \cdot tg\alpha$

For R use the value R = 1.987 cal $mole^{-1}$ K^{-1}.

- *Present the results in tabular form*

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Table V.15-1 Experimental data

Boiling - tube	$\ln x_2^{sat}$	t (^{0}C)	T (K)	1/T (K^{-1})	tgα (K)	ΔH_{dis}^{sat} (cal $mole^{-1}$)
1	-2.2996					
2	-1.7384					
3	-1.4528					
I	-0.7131					
II	-0.5098					
III	0	80.2				

CONCLUSIONS AND DISCUSSIONS

- Interpret the obtained results;
- Other systems, which can be studied: Na_2SO_4 in water, KCl in water etc.

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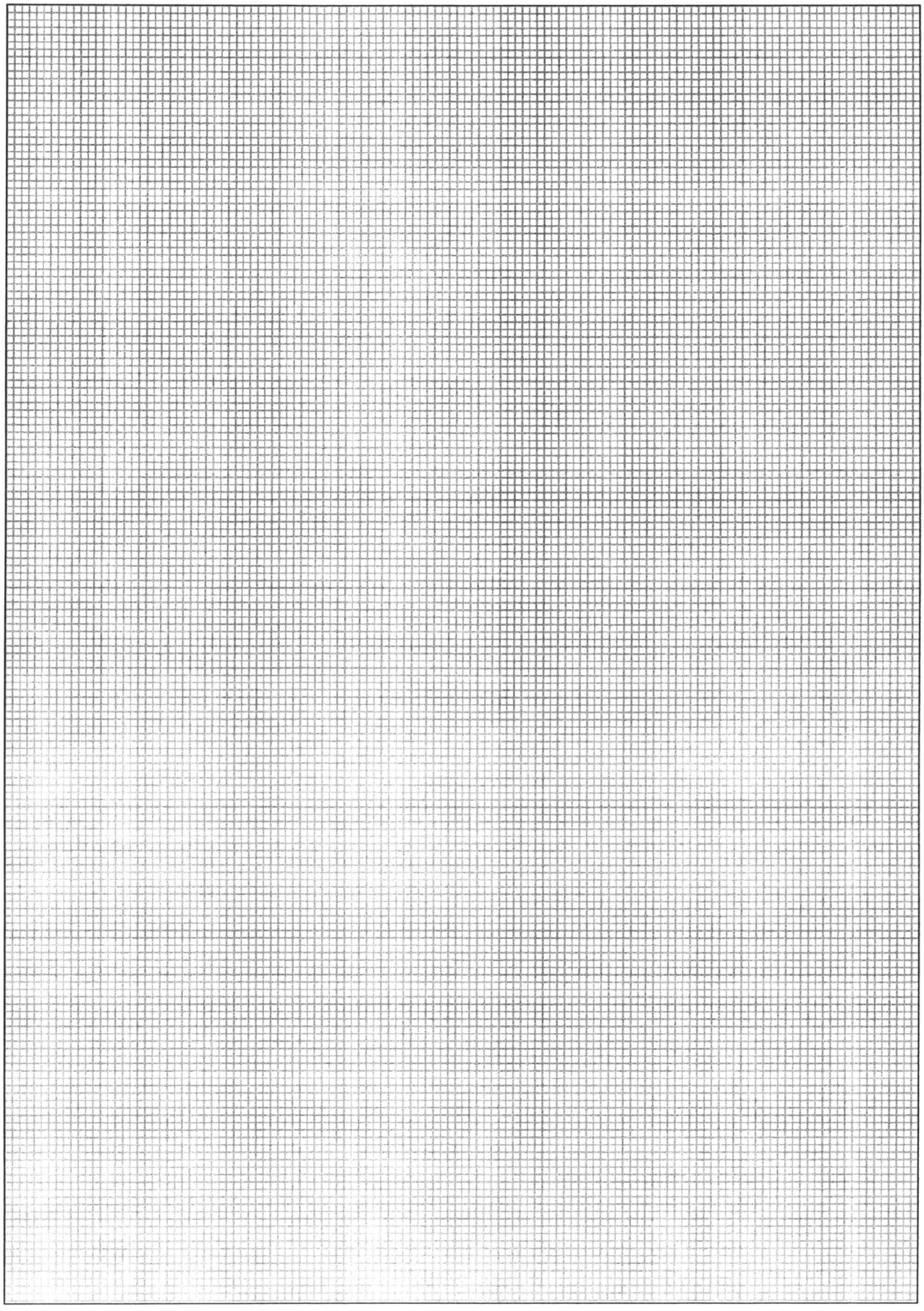

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V.16. DETERMINATION OF MOLECULAR WEIGHTS AND ACTIVITY COEFFICIENTS

Dilute solutions plays an important role in chemical thermodynamics because many of their properties are found to be closely related to the molar concentration of solute, which they contain, and depend relatively little on the nature of solute. Consequently, measurements of these properties have provided methods of determining molecular weights of substances in solution.

When a substance C_2 is dissolved in a solvent C_1, the vapor pressure of C_1 is reduced from its normal value P_1^0 to a lower value P_1 which is given according Raoult's Law by $P_1 = P_1^0 x_1^l$ where x_1^l is the mole fraction of C_1 in the solution.

In practice, Raoult's Law is found to hold approximately for solution in which solute and solvent are of very similar chemical nature. More often, however, Raoult's Law holds only for the solvent, C_1, and then only for solutions that are very dilute in C_2 (i. e. $x_1^l \rightarrow 1$). In such solutions, the solute C_2 tends to follow Henry's Law, namely $P_2 = k\, x_2^l$ or $P_2 = P_2^0\, x_2^l\, f_2^l$, where f_2^l is the fugacity coefficient.

If G_2 grams of solute with unknown molecular weight M_2 are dissolved in G_1 grams of solvent with known M_1 molecular weight, the partial pressure of C_1 over the solution is given by:

$$P_1 = P_1^0 \cdot \frac{G_1/M_1}{\left(G_1/M_1 + G_2/M_2\right)} \qquad \text{(V.16-1)}$$

if the solution is ideal. Consequently, ***a study of the vapor pressure of the solvent*** can give information about the molar composition of the solution and if the weight composition is known, the molecular weight of the solute can be calculated. The lowering of the vapor pressure can be measured by the gas saturated method, by a dew-point method or by the isopiestic method in which the solution is brought to vapor equilibrium with solution of the substance of known vapor pressure. These methods are frequently used for studying the thermodynamic properties of solutions, but they are rarely employed for molecular weights determinations.

In place of the lowering of vapor pressure it is more convenient to measure the ***elevation of the boiling point*** θ_e or ***depression of freezing point*** θ_c. The origin of these phenomena can be understood from the vapor pressure diagram (figure V.16-1).

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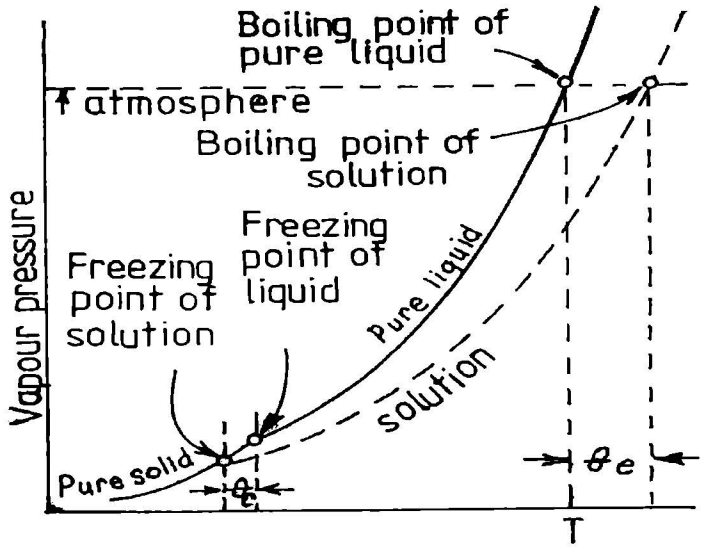

Figure V.16-1. Diagram showing the effect of a non-volatile solute in reducing the vapor pressure, raising the boiling point and depressing the freezing of a solution

The solution having a lower vapor pressure than the pure solvent (assuming solute C_2 to be more non-volatile) must be raised to a higher temperature to bring its pressure up to 1 atm, i. e. its boiling point, and similarly the solution must be cooled to a lower temperature for its vapor pressure to coincide with that of the pure solid (i. e. its freezing point). It can be shown by thermodynamics that the elevation of the boiling point (the solute being non-volatile) or depression of the freezing point (assuming that pure solvent crystallizes out on cooling) for a dilute solution in which the solvent obeys Raoult's Law are given by the same formula, namely:

$$\theta_e = \frac{R \cdot \left(T_1^0\right)^2}{\frac{\Delta^v H_1^0}{M_1} \cdot 1000} \cdot m \qquad \theta_c = \frac{R \cdot \left(T_1^0\right)^2}{\frac{\Delta^t H_1^0}{M_1} \cdot 1000} \cdot m \qquad \text{(V.16-2)}$$

where θ_e and θ_c are the elevation of the boiling point, respectively the depression of freezing point, $\Delta^v H_1^0$ is the molar heat of vaporization, $\Delta^t H_1^0$ is the molar melting heat and T_1^0 is the normal boiling (or freezing) point on the Kelvin scale. On rearrangement, the equation (V.16-2) gives the molecular weight of the solute:

$$\theta_e = k_e \cdot m = k_e \cdot \frac{1000 \cdot G_2}{M_2 \cdot G_1} \qquad \theta_c = k_c \cdot m = k_c \cdot \frac{1000 \cdot G_2}{M_2 \cdot G_1} \qquad \text{(V.16-3)}$$

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$$M_2 = k_e \cdot \frac{1000 \cdot G_2}{\theta_e \cdot G_1} \qquad M_2 = k_c \cdot \frac{1000 \cdot G_2}{\theta_c \cdot G_1} \qquad \text{(V.16-4)}$$

where k_e is the ebullioscopic constant, k_c is the cryoscopic constant, both being properties of the pure solvent; m is the molal concentration of the solution.

Table V.16-1 gives the approximate values of these constants for some common solvents.

Table V.16-1

Solvent	t_t (^{0}C)	k_c	t_f (^{0}C)	k_e
Acetic acid	16.6	3.900	-	-
Acetone	-	-	56.2	1.710
Benzene	5.4	5.120	80.2	2.530
Chloroform	-	-	61.2	3.630
Etyl alcohol	-	-	78.5	1.220
Nitrobenzene	5.3	7.200	-	-
Water	0.0	1.858	100.0	0.505

The freezing point depression is easier to measure accurately than is the boiling point elevation. It has therefore been used frequently for studying the behavior of solutes which give abnormal results for molecular weights on account of *association* (e. g. carboxylic or hydroxy-compounds in benzene), *dissociation* (e. g. salts in water), hydration, or complex formation. Ideally, the method provides means of counting the total number of molecules or ions in the solution, since θ_c gives x_2', the mole fraction, but the theory is limited to solutions, which are more or less ideal. Electrolytes, in particular, are grossly non-ideal because the coulombic interaction between the ions has an important influence even in dilute solutions, and consequently the above theory does not hold. Instead, measurements of freezing point depression are used to study the activity coefficients of electrolyte solutions (for detailed informations see: "Termodinamică chimică", Rodica Vîlcu, Editura tehnică, Bucureşti 1994, pag. 621-625).

Another property, which is closely related to those discussed above, is ***osmotic pressure***. This is the hydrostatic pressure, which must be applied to the solution to bring its vapor pressure up to that of the normal pure solvent. The osmotic pressure of very dilute, ideal solutions is given by the relation:

$$\pi = R \cdot T \cdot c = R \cdot T \cdot \frac{n}{V} \qquad \text{(V.16-5)}$$

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where n is the number of moles of solute dissolved in a solution of volume V. Osmotic pressure therefore provides another means of determining molecular weights. The technique – especially the preparation of semi-permeable membranes – is difficult and outside the scope of this book. The method is used for high polymers and proteins. The relation performs the calculation of molecular weight:

$$\pi = R \cdot T \cdot \frac{G_2 / n_2}{V} \qquad M_2 = \frac{R \cdot T \cdot G_2}{\pi \cdot V} \qquad \text{(V.16-6)}$$

where G_2 represents the mass of solute contained in the solution of volume V.

An important and new method of determining molecular weights is the *scattering of light* by solutions that can be related to their osmotic pressure.

EXPERIMENTAL METHODS

I. Elevation of boiling point

The true boiling point of a liquid is the temperature at which its vapor and liquid are in equilibrium under a pressure of 1 atm. This temperature cannot be determined accurately by simply inserting a thermometer into the boiling liquid, as the temperature in the liquid is variable and too high on account of local superheating and the effect of hydrostatic pressure. In the case of a *pure* liquid the *condensation* temperature can be determined instead by placing a thermometer in the condensing vapor, but in the case of solutions this method is not applicable since the condensation temperature then differs from the boiling point owing to fractionation.

One solution to the problem is to heat the liquid to its boiling point by means of a current of vapor. This method eliminated superheating, but the concentration of the solution is thereby altered and must be determined subsequently.

All modern forms of apparatus make use of a principle introduced by Cotrell; the thermometer is hung *in the vapor* above the boiling solution and a stream of boiling liquid is sprayed by a simple pump on the thermometer *above the bulb*. The liquid is slightly superheated (e. g. by about 0.05^0) when it emerges from the pump, but in flowing down the thermometer is very quickly comes to equilibrium with the surrounding vapor, cooling slightly by evaporation. The liquid dripping from the bulb is therefore at its true boiling point.

Two forms of boiling point apparatus, or ebulliometers, are shown in figure V.16-2: (a) is the apparatus of Washburn and Read and (b) is the ebulliometer of Swietoslawski.

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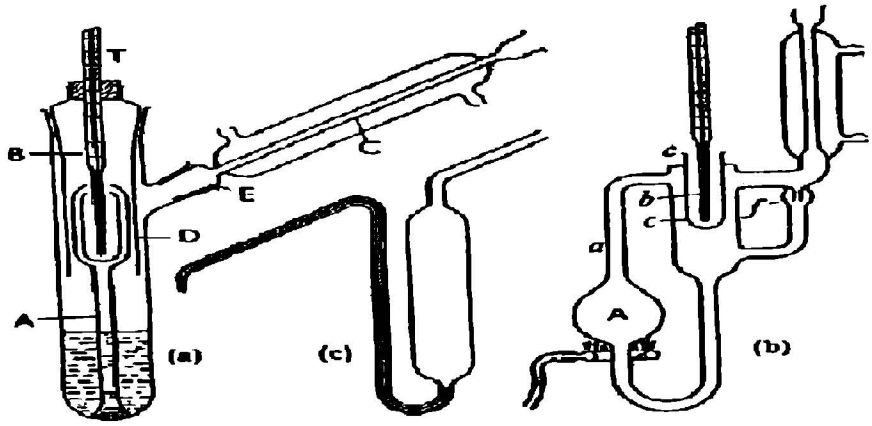

Figure V.16-2. Determination of elevation of the boiling point
(a) Apparatus of Washburn and Read, (b) Apparatus of Swietoslawski, (c) Weight delivery pipette

In both types of apparatus the boiling liquid is carried upwards by the stream of vapor bubbles through a narrow tube A, so that liquid squirts continually on the thermometers steam B or inserted well c into which the thermometer is dipped. In the former apparatus the lift divides in two or three branches symmetrically arranged round the thermometer. The tube D is to act as a radiation screen round the thermometer and to keep off cold liquid which may run down the condenser C. Swietoslawski's ebulliometer incorporates a drop-counter f which indicates the rate at which the liquid is distilling. Although originally heated by gas, either ebulliometer can be adapted for electric heating, and this has the advantage of being less disturbed by draughts, and gives closer regulation and reproducibility.

II. Depression of freezing point

The principle of this method is to find the arrest that occurs in the cooling curve of the solution, corresponding to the onset of crystallization of solid. A freezing mixture cools the solution very slowly. Crystallization usually does not begin until the temperature has fallen a little below the true freezing point, i. e. the solution supercools, but as soon as nucleation has taken place the latent heat of crystallization tends to raise the temperature. The temperature cannot rise above the freezing point, but

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if the cooling is too rapid it may well never reach the true melting point. The proper experimental technique must therefore be adhered to closely to obtain reliable results.

The apparatus is shown in figure V.16-3. The inner test tube (A) containing the solution, stirrer (B) and thermometer (C), is partially insulated from the surrounding cooling bath (F) (a ice-salt or better a cryostat), being suspended in a larger test tube (D) with an air space (E) in between.

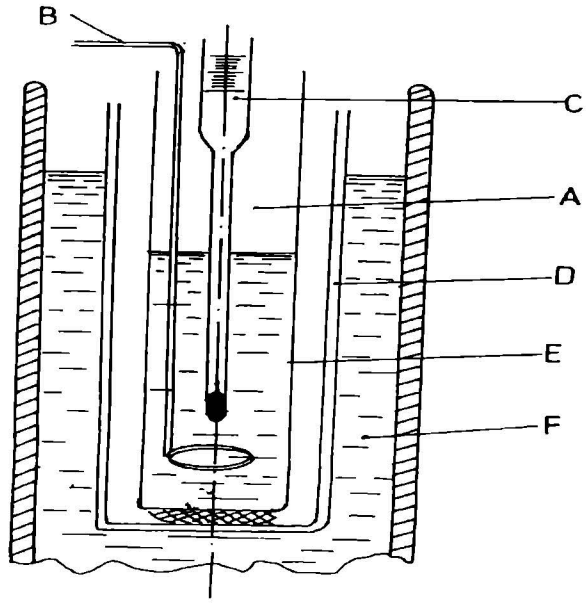

Figure V.16-3. Apparatus for cryoscopic determination of molecular weight

The thermometer is a Beckmann thermometer with a 5^0 range adjusted to cover the temperature range expected in the experiment.

Precautions which should be observed in carrying out determinations by the method:

- the temperature of the cooling bath must not be too low, otherwise the supply of heat by crystallization of the solvent may not be great enough to counteract the abstraction of heat by the cooling bath (not more than 3^0 or 4^0 below the freezing point of the liquid);
- the amount of supercooling should not exceed $0.3 - 0.5^0$. If a larger amount of supercooling occurs, the solution can be seeded by adding a small crystal of frozen solvent;
- the stirring should not be too rapid and should be as uniform as possible otherwise too much heat is generated.

As an example of cryoscopic method application for the determination of activity coefficients we can use for this study aqueous solutions of KCl at molal concentrations in the range: $0.1 \div 1$ molal.

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In order to obtain correct values for cryoscopic depression, θ_c, the Beckmann thermometer must be calibrated so that the upper end of mercury to be near value 5 of the scale. Several measurements for establishing of freezing point of water will be made taking into account that an error in this measurements will affect each value of freezing temperature of solutions.

For KCl solution: $m_0 = 0.1000$, $\gamma_0 = 0.798$.

III. Osmotic pressure

Macromolecules are very large molecules with molecular weights ranging in order of magnitude from 1000 to 1000000 or more. They are, with a few exceptions, organic molecules and many examples such as cellulose and starch exist in nature. Macromolecules can be made synthetically. These are called high polymers because structurally they are formed by the linking together of monomers units to form chains of considerable length.

From measurements of the osmotic pressure of dilute solutions of a polymer, the average molecular weight of the polymer can be obtained, since π is of the order of several Torr even for very dilute solutions. The other colligative properties – freezing point depression, boiling point elevation and vapor-pressure lowering – show effects which are two small for accurate measurements; typical values for dilute high-polymer solutions would be $5x10^{-4}$ ^{0}C, 10^{-4} ^{0}C and 10^{-4} Torr, respectively.

There are two methods for osmotic pressure measurements.

In the ***dynamic-equilibrium method***, applying an external gas pressure to the solution can prevent flow of solvent through the membrane; the equilibrium pressure, which is necessary to obtain zero flow, will equal the osmotic pressure. Although this method is rapid, it involves a complex cell, which must be leaktight.

In the ***static method***, solvent is allowed to diffuse through the membrane until there is no further change in the internal head. It is necessary to correct this head for the effect of surface tension (capillary rise) and to calculate the equilibrium concentration of the solution, which will differ from the initial concentration due to passage of solvent through the membrane. The disadvantage of this method is that it is slow, equilibrium usually requiring several days.

In both techniques, the osmotic pressure is determined from the internal head of solution in a capillary tube on the solution side of membrane.

In figure V.16-4 is presented a scheme of a simple osmometer.

This osmometer consists of a small, heavy-wall cylindrical cell with a filling tube and a 0.5-mm inner diameter measuring capillary sealed into its side. The open ends of the cell are ground flat and

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smooth, so that the membrane, which is held in place by perforated metal plates, also serve as gaskets. Attached to the measuring capillary is a short length of capillary with the same inside diameter. This is immersed in the solvent to provide a correction for capillary rise.

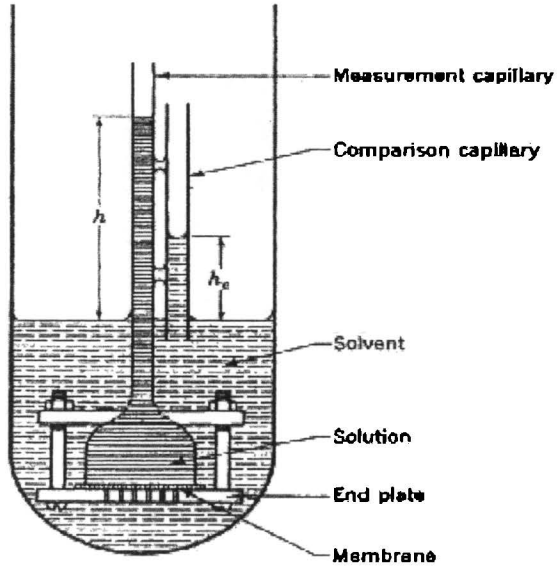

Figure V.16-4. A simple osmometer; $\Delta h = h - h_c$ is the internal head corrected for capillary rise

Membranes

Of the many materials used for membranes the most convenient one is cellulose in the form of non-waterproofed cellophane sheet. Cellophane is a good membrane for methyl ethyl ketone, and can be prepared in a range of porosities by treatment with strong basis solutions. Polystyrene is a suitable polymer for investigation in methyl ethyl ketone solvent. It is necessary to have a reasonably high molecular weight fraction to avoid diffusion of solute molecules through the membrane. If such solute diffusion occurs, the osmotic pressure will change with time. Membranes should be stored in the solvent and never allowed to dry out.

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V.17. A STUDY OF THE TERNARY SYSTEM BENZENE – METHANOL – WATER

This experiment will determine the limit of homogeneous phase in the system benzene – methanol – water.

Gases are miscible in all proportions, but other phases more often show only partial miscibility. One often needs to know the solubility of a gas in a liquid or solid, of a liquid in another liquid, or of a solid in a liquid.

Three component liquid systems

The mutual solubility of a pair of partially miscible liquids may be markedly altered by the addition of a third component. In general, when a third component is soluble in only one of the other two components, the mutual solubility of the two liquids is diminished; but when the third component dissolves readily in each of the other two components, the mutual solubility of the latter is increased. The system benzene –methanol – water illustrates this behavior. When methanol is added to a heterogeneous mixture of benzene and water at a definite temperature, the mutual solubility of these two liquids is increased, and a point is reached at which the mixture becomes homogeneous. The amount of methanol, which must be added to bring about homogeneity at a given temperature, will depend on the relative proportions of benzene and water in the original mixture. Similarly, when benzene is added to a homogeneous mixture of water and methanol (two completely miscible liquids), a heterogeneous mixture (two liquid solutions) is formed with a certain amount of benzene, depending on the initial composition of the mixture has been added.

METHOD

For a three component system at constant temperature and pressure, the phase rule ($F = C - P + 2$) reduces to:

$$F = 3 - P$$

The composition of such a system may be expressed in terms of the co-ordinates of an equilateral triangle (or the triangular diagram), each apex corresponding to a pure component.

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Method of determine triangular diagram consists in preparation of some mixtures of benzene and water (heterogeneous mixtures) of varying composition and the addition of a third liquid – methanol (in a way like a normal titration). The third component (CH_3OH) is soluble in each layer and on addition to a mixture of benzene and water distributes itself between these layers. The composition of the layers changes as more methanol is added. Under these conditions, P equals 2, and the system is completely defined by the composition. Thus if the points corresponding to these compositions are plotted, a smooth curve may be drawn indicating the limits of miscibility of water – benzene mixtures in methanol.

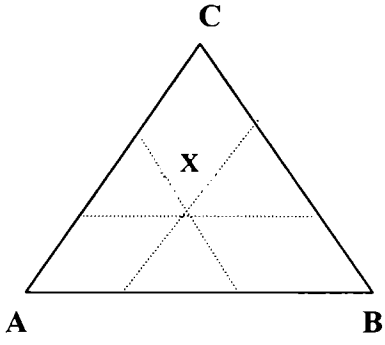

Figure V.17-1 Representation of the composition of a ternary mixture by means of triangular co-ordinates

It will be noted that as more and more methanol is added, the water and benzene solutions become more and more miscible until complete miscibility is achieved. This solubility curve is known as a binodal curve. Any mixture within the area enclosed by this binodal curve and the base of the triangle will resolve into two liquid layers and any mixture outside the area will form only one liquid layer. The position of this curve changes with the temperature.

APPARATUS AND CHEMICALS

- Three burettes, two dried 250-ml Erlenmeyer flasks;
- Distilled water, pure benzene and methanol.

EXPERIMENTAL

Two series of experiments will be performed.

-In series I, in one of 250-ml Erlenmeyer flask add 10 ml of distilled water. From the burette that contains benzene add 0.5 ml and shake well. You can easily observe that two layers are obtained. Fill the burette with methanol till indication zero. Start addition of methanol on vigorously shaking until turbidity appears. The final additions of methanol should be made drop by drop (care being taken not to add too much methanol) until the system becomes homogeneous. The corresponding value of

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volume of added methanol should be noted in table V.17-1. In the same conical flask add another volume of C_6H_6 (till the volume of methanol becomes 1 ml – it means to add another 0.5 ml). The system again becomes heterogeneous. From the burette with methanol add carefully on shaking until the system becomes homogeneous again. Record the final volume of methanol (the volume of methanol is additive) and write its value in the table V.17-1. Then add another volume of benzene (1 ml), shake well and continue to add CH_3OH and so on (follow the indications from the table V.17-1).

-In series II, in the second 250-ml Erlenmeyer flask, put from the beginning 10 ml of benzene and from the burette containing water add 0.5 ml. Refill the burette with methanol (till the indication zero) and start to add methanol until the system becomes homogeneous. Follow the similar procedure like in series I experiments and accordingly with the indications from table V.17-1.

Finally, on the proportion 10 ml H_2O - 10 ml C_6H_6, the same value of methanol volume should be obtained.

CALCULATIONS

- *From the amount of methanol added and the initial amounts of water and benzene, the percentage composition (in volume) of the mixture when system becomes homogeneous is calculated, and results are written in table V.17-1;*
- *Plot the results in a triangular diagram. The obtained points are joined by a smooth curve.*

Table V.17-1 Experimental data

	Series I								**Series II**							
A-H_2O (ml)	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**0.5**	**1**	**2**	**3**	**4**	**6**	**8**	**10**
B-C_6H_6 (ml)	**0.5**	**1**	**2**	**3**	**4**	**6**	**8**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
C-CH_3OH (ml)																
%A																
%B																
%C																

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The triangular diagram

A triangular diagram usually consists of an equilateral triangle. The length of the side is taken as unity or 100 (10 cm) and represents, therefore, the sum of the fractional or percentage amounts of the three components; each corner of the triangle represents 100% of one of the components (fig. V.17-1). In plotting the composition of ternary mixture, two points are marked on one side of the triangle, representing the percentage amounts of two components, and from these points lines are drawn parallel to the other two sides of the triangle. The point of intersection gives the composition of the ternary mixture. Printed triangular co-ordinate graph paper is obtainable (for more explanations see also chapter IV.e).

CONCLUSIONS AND DISCUSSIONS

- The curve obtained by joining the experimentally determined points forms the boundary between homogeneous and heterogeneous mixture. A mixture of benzene – methanol – water represented by any point *outside* the curve, towards the methanol corner of the triangle, will form only one homogeneous solution, while any mixture represented by a point *within* the curve will separate into two layers;
- If it is required to draw tie – lines across the miscibility gap to indicate conjugate solutions, pairs of mutually saturated solutions must be analyzed. Since the binodal curve has been determined in the above experiment it will suffice to analyze for CH_3OH only;
- *Additional experiments:* the system benzene – methanol – water was studied at room temperature in a manner described above. Further, the boundary curve of this system may be determined at a series of temperatures and the curves plotted on the same triangular diagram. The construction of a three-dimensional model would also be instructive.

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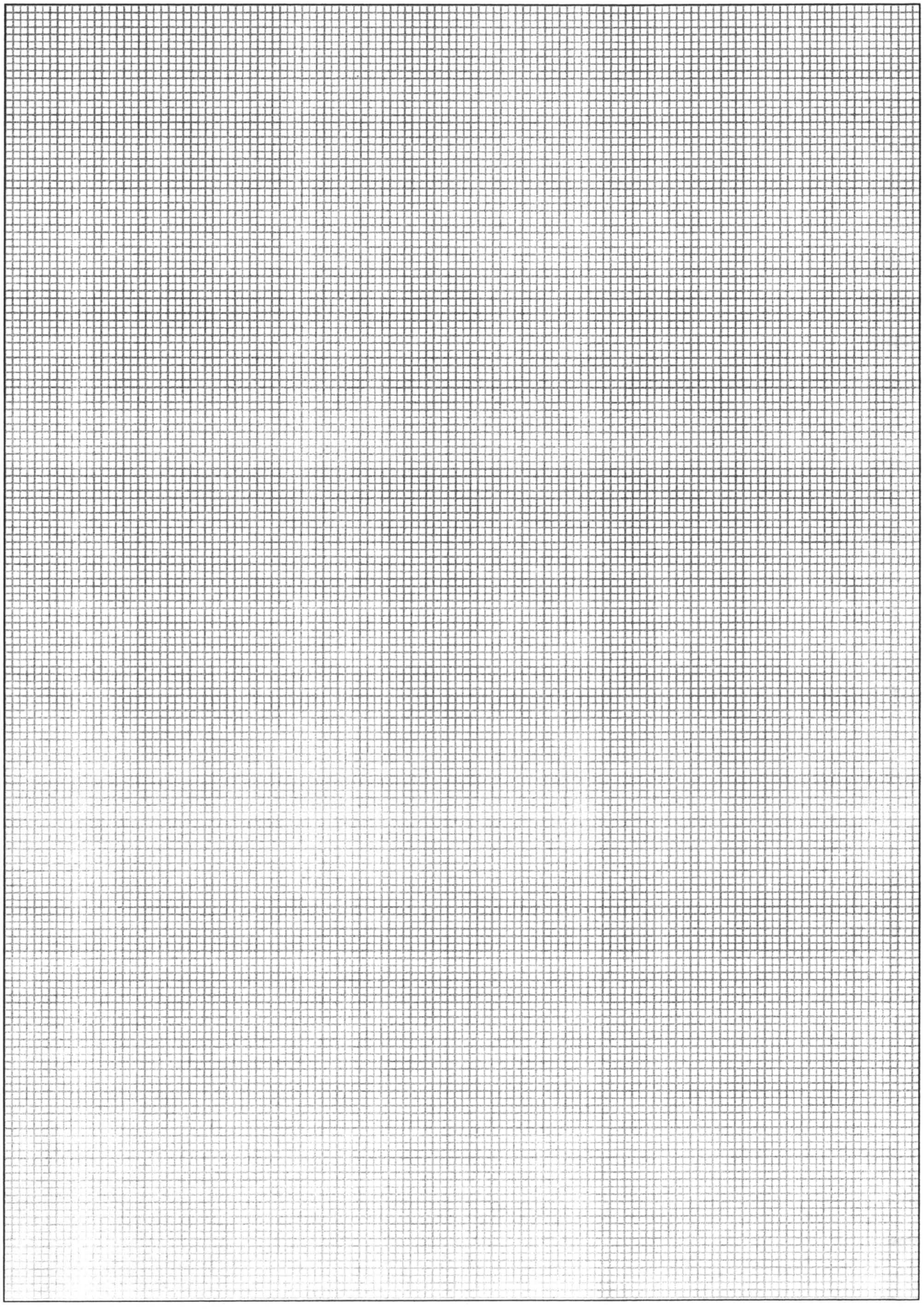

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VI. NUMERICAL APPLICATIONS

VI.1 A non-ideal solution contains n_A moles of A component and n_B moles of B component. The free energy of the solution is given by the equation:

$$G = n_A \cdot \mu_A^0 + n_B \cdot \mu_B^0 + RT \cdot (n_A \cdot \ln x_A + n_B \cdot \ln x_B) + C \cdot \frac{n_A \cdot n_B}{n_A + n_B}$$

Deduce the expression of chemical potential of A component.

R: $\mu_A = \mu_A^0 + RT \cdot \ln x_A + C \cdot x_B^2$

VI.2 The molar volume of two miscible liquids, A and B can be expressed by the equation:

$$V = a + b \cdot x_B - c \cdot x_B^2$$

in which the coefficients a, b and c are positive.

a) Calculate the molar volumes of pure components A and B;

b) Calculate the partial molar volumes of A and B at $x_B = 0.4$.

R: $V_A^0 = a;\ V_B^0 = a + b - c;\ \overline{V}_A = a + 16 \cdot c;\ \overline{V}_B = a + b - 0.64 \cdot c$

VI.3 At 0^0C, the density, ρ, of aqueous solutions of $Ca_2[Fe(CN)_6]$ can be represented by the equation:

$$\rho = 1.00 - 0.245 \cdot c - 0.0215 \cdot c^2$$

in which c is the molar concentration. Calculate the partial molar volumes of water, $\overline{V}_1$, and of $Ca_2[Fe(CN)_6]$, $\overline{V}_2$, at c = 1 mole/l.

R: $\overline{V}_1 = \dfrac{M_1}{\rho - c \cdot \dfrac{\partial \rho}{\partial c}} = 17.62\ ml \cdot mole^{-1}$ $\qquad$ $\overline{V}_2 = \dfrac{M_2 - 1000 \cdot \dfrac{\partial \rho}{\partial c}}{\rho - c \cdot \dfrac{\partial \rho}{\partial c}} = 567.79\ ml \cdot mole^{-1}$

VI.4 The volume of aqueous solution of KCl at 25^0C is given by the equation:

$$\mathbf{V} = 1002.94 + 27.17 \cdot m + 1.744 \cdot m^2$$

where **V** is the volume (cm^3) of a solution with 1000 g H_2O and m moles of KCl. Establish expressions for partial molar volumes of water and KCl as function of molality.

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R: $\overline{V}_1 = 18.06 - 0.0314 \cdot m^2$; $\overline{V}_2 = 27.17 + 3.488 \cdot m$

VI.5 For the solute (2) in dilute solutions in a certain solvent, the partial molal volume is given by the equation: $\overline{V}_2 = a + b \cdot m$, where m is the molality of the solution and a and b are constants. Express the partial molal volume $\overline{V}_1$ in terms of a, b, m and quantities characteristic of the solvent.

R: $\overline{V}_1 = V_1^0 - \frac{M_1 \cdot b \cdot m^2}{2000}$

where M_1 and V_1^0 represent the molar mass and molar volume of pure solvent.

VI.6 The compressibility factor $Z = PV/RT$ for CO_2 at 0^0C and 100 atm is equal to 0.2007.

Calculate the volume occupied by 0.1 moles of gas at 0^0C and 100 atm.

R: $V = 4.50 \times 10^{-3}\ l$

VI.7 For a gas, which obey to van der Waals equation:

$V_c = 3 \cdot b$; $P_c = a/27 \cdot b^2$; $T_c = 8 \cdot a/27 \cdot R \cdot b$. Calculate the compressibility factor.

R: $Z_c = 0.375$

VI.8 The experimental value of RT/V is 1.10 for 1 mole of a certain non-ideal gas. The gas is at 1 atm and its temperature is below the critical temperature. If the pressure is not halved, at constant temperature, it is to be expected that the new volume will be (more than twice, less than twice) the original volume.

R: $PV/RT = 1/1.10 = 0.9$.

The compressibility factor will increase as pressure is reduced; hence the new volume will be more than twice the original

VI.9 A non-ideal gas of molecular weight 150 obeys to van der Waals equation; its critical pressure and temperature are 100 atm and 100^0C, respectively.

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a) The compressibility factor will be greater that unity at: 500 atm and 80^0C; 5000 atm and 120^0C: 50 atm and 120^0C; none of this:

b) Calculate the value of compressibility factor at the critical point.

R: a) Z > 1 at 5000 atm and 120^0C; b) $Z_c = \frac{P_c \cdot V_c}{R \cdot T_c} = \frac{3}{8} = 0.375$

VI.10 Doubling the temperature at constant pressure will (more than, less than) double the volume of a gas if the gas is: ideal, non-ideal and below T_c, non-ideal and above its Boyle temperature, non-ideal at low pressure.

R: When $V_f = 2V_{in}$ or $V_f = V_{in}/2$ the gas can be ideal. If the gas is non-ideal and below T_c, V will more than double. If it is above its Boyle temperature, the doubling of T, decrease Z and V will less than double. At low pressure gases approach ideality.

VI.11 Calculate the heat effect of the reaction: $NH_3(g) + \frac{5}{4} \cdot O_2(g) = NO(g) + \frac{3}{2} \cdot H_2O(g)$ according to the following data:

$H_2O(g) = H_2O(g)$	(1)	$\Delta H_1 = -10519\ cal \cdot mole^{-1}$
$\frac{1}{2} \cdot N_2(g) + \frac{3}{2} \cdot H_2(g) = NH_3(g)$	(2)	$\Delta H_2 = -11040\ cal \cdot mole^{-1}$
$H_2(g) + \frac{1}{2} \cdot O_2(g) = H_2O(l)$	(3)	$\Delta H_3 = -68315\ cal \cdot mole^{-1}$
$NO(g) = \frac{1}{2} \cdot N_2(g) + \frac{1}{2} \cdot O_2(g)$	(4)	$\Delta H_4 = -21570\ cal \cdot mole^{-1}$

R: $\Delta H = -54084\ cal \cdot mole^{-1}$

VI.12 Calculate the thermal effect of the reaction: $NH_3(g) + \frac{5}{2} \cdot O_2(g) \rightarrow NO(g) + \frac{3}{2} \cdot H_2O(g)$

$H_2O(g) \Leftrightarrow H_2O(l)$	(1)	$\Delta H_1 = -10.520\ kcal \cdot mole^{-1}$
$\frac{1}{2} \cdot N_2(g) + \frac{3}{2} \cdot H_2(g) \Leftrightarrow NH_3(g)$	(2)	$\Delta H_2 = -11.040\ kcal \cdot mole^{-1}$
$H_2(g) + \frac{1}{2} \cdot O_2(g) \Leftrightarrow H_2O(l)$	(3)	$\Delta H_3 = -68.320\ kcal \cdot mole^{-1}$
$NO(g) \Leftrightarrow \frac{1}{2} \cdot N_2(g) + \frac{1}{2} \cdot O_2(g)$	(4)	$\Delta H_4 = -21.600\ kcal \cdot mole^{-1}$

R: $\Delta H = -54.060\ kcal \cdot mole^{-1}$

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VI.13 For the reaction: $H_2S(g)+\frac{3}{2}\cdot O_2(g)\rightarrow H_2O(g)+SO_2(g)$ the following data are known:

Compound	$H_2S(g)$	$O_2(g)$	$H_2O(g)$	$SO_2(g)$
$\Delta H^0_{298}\left(kcal\cdot mole^{-1}\right)$	-4.815	0	-57.7979	-70.96

And the expression for variation of heat capacity for the reaction is:

$\Delta C_P = -2.162 + 5.634\times10^{-3}\cdot T \quad (\text{between } 298\text{-}1500\,\text{K})$

a) Find ΔH^0 and ΔE^0 at 25°C;

b) Find ΔH^0 at 1000 K

c) Do you have enough information to find ΔH^0 at 2000 K? Explain.

R: $\Delta H^0_{298} = -123.94\ kcal\cdot mole^{-1}; \Delta E^0_{298} = -123.64\ kcal\cdot mole^{-1}$

$\Delta H^0_{1000} = -122.58\ kcal\cdot mole^{-1}$; No, the given data apply only to the range 298 to 1500 K

VI.14 The heat of vaporization of formic acid at normal boiling point (100.6°C) is 177.6 cal·g^{-1}, and the heat of vaporization of ethanol at normal boiling point (78.3°C) is 195.3 cal·g^{-1}.

a) Show the differences comparatively with Trouton's law.

b) Explain the phenomenon.

R: $\Delta^v S_{(HCOOC)} = 14.5\ cal\cdot mole^{-1}\cdot K^{-1}; \quad \Delta^v S_{(CH_3OH)} = 25.6\ cal\cdot mole^{-1}\cdot K^{-1}$

The results show the association between molecules of formic acid (in vapor phase) and ethanol (in liquid phase).

VI.15 Explain why it is permissible to omit the concentration of pure solids and liquids in calculation K_c for a heterogeneous reaction.

R: The standard state for a solid, or a liquid that appears pure or as a solvent, is the pure substance: $\mu = \mu^0 + RT\ln a$. In this case, $\mu = \mu^0$ and $a = 1$. Thus we replace each activity of a pure substance by 1 in the equilibrium condition, which is equivalent to omitting it. If the substance is not quite pure, a first approximation to the activity is the mole fraction (according to Raoult's Law), not the concentration.

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VI.16 For a certain element the heat capacity of the solid is: $C_P^s = a + b \cdot T \ (cal \cdot mole^{-1} \cdot K^{-1})$ and the heat capacity of a liquid is: $C_P^s = e + f \cdot T \ (cal \cdot mole^{-1} \cdot K^{-1})$ where a, b, e, f are all constants. The standard enthalpy of fusion at temperature T_1 and $\Delta H_1^0 \left(cal \cdot mole^{-1}\right)$ is ΔG_1^0. Derive the equation of free energy ΔG^0 as function of temperature.

R: $\Delta G^0 = \frac{T \cdot \Delta G_1^0}{T_1} + \Delta H_1^0 \cdot \left(1 - \frac{T}{T_1}\right) + (e-a) \cdot \left(T \cdot \ln \frac{T_1}{T} + T - T_1\right) - \frac{1}{2} \cdot (f-b) \cdot (T - T_1)^2$

VI.17 The dissociation pressure of the system: $Ca(OH)_2(s) \Leftrightarrow CaO(s) + H_2O(g)$, is 10.5 mm Hg at 340.6^{0}C and 101.2 mm Hg at 421.3^{0}C. Calculate the mean heat of hydration of calcium oxide over this temperature range.

R: $\Delta H = -23.76 \ kcal \cdot mole^{-1}$

VI.18 At 30^{0}C, the butyric ether of liquid metacrilic acid ($C_8H_{14}O_2$) has a density equal to 0.88601 g·cm^3. Calculate the variation of free energy when 1 mole of this substance is compressed from 1 atm to 20 atm.

R: $\Delta G = 73.78 \ cal \cdot mole^{-1}$

VI.19 Establish an equation for ΔG^0 for the reaction $I_2(s) \Leftrightarrow 2 \cdot I(g)$ knowing that I(g) is a monoatomic gas with an ideal behavior and heat capacity for I_2 is given by the expression:

$C_{P_{I_2}} = 7.4 + 10^{-3} \cdot T$

R: $\Delta G^0 = \Delta H_0 - 2.6 \cdot T \cdot \ln T + 0.5 \cdot 10^{-3} \cdot T^2 + I \cdot T$

VI.20 The vapor pressure of a certain pure liquid is given by the equation: $\ln P(g) = A + B \ln T + \frac{C}{T}$

and the vapor pressure of the corresponding solid is: $\ln P(s) = A' + B' \ln T + \frac{C'}{T}$.

a) Express the molar heat of vaporization of the liquid, $\Delta^v H(l)$ and of the solid $\Delta^f H(s)$ in terms of any or all of A, B, C, A', B', C' and T;

b) Express the molar heat of fusion in terms of the same quantities;

c) Express similarly the difference in molar heat capacities between liquid and solid;

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d) Write one equation that could be solved for the melting point of the substance if (A, B, C, A', B', C') were known.

R: $\Delta^v H = R \cdot (BT - C); \Delta^f H = R \cdot [(B'-B)T - (C'-C)];$

$$C_P(l) - C_P(s) = R \cdot (B'-B); \ln P(l) = \ln P(s) \Rightarrow A + B \ln T + \frac{C}{T} = A' + B' \ln T + \frac{C'}{T}$$

VI.21 Solid cupric bromide vaporize according to the equation:

$2 \cdot CuBr_2(s) \Leftrightarrow 2 \cdot CuBr(s) + Br_2(g)$

In the temperature range $50 \div 110^0$C, the vapor pressure is given by the following equation:

$$\log P(mmHg) = -\frac{5056}{T} + 12.01$$

Assuming that this expression may be extrapolated to 25^0C, evaluate the equilibrium constant ΔG^0, ΔH^0 and ΔS^0 for the reaction at 25^0C. The activity of the solid phases may be set equal to unity.

R: $K = 1.1 \times 10^{-5}$ mm Hg = 1.4×10^{-8} atm; $\Delta G^0 = 10.7$ kcal·mole^{-1}; $\Delta H^0 = 23.1$ kcal·mole^{-1}; $\Delta S^0 = 41.6$ cal·mole^{-1}·deg^{-1}.

VI.22 The dissociation pressure of $CaCO_3$ is 626 mm Hg at $t_1 = 892^0$C and 775 mm Hg at $t_1 = 910^0$C. Calculate the heat of the reaction: $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$.

R: 32726.48 cal·mole^{-1}

VI.23 At 30^0C, the butyric ether of liquid metacrilic acid ($C_8H_{14}O_2$) has a density equal to 0.88601 g·cm^3. Calculate the variation of free energy when 1 mole of this substance is compressed from 1 atm to 20 atm.

R: $\Delta G = 73.78 \ cal \cdot mole^{-1}$

VI.24 Indicate precisely the conditions under which the formula $F = C + 2 - P$ is valid.

R: The formula is valid for a system at equilibrium in which phase concentration plus two other properties of state can be varied.

VI.25 Why it would be incorrect to apply the formula: $\ln \frac{P_2}{P_1} = \frac{\Delta H}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ to phase equilibrium:

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$C(diamond) \Leftrightarrow C(graphite)$?

R: In the derivation of the given formula it is assumed that one of phase is an ideal gas and that the molar volume of one of the phases is negligible small in comparison with the molar volume of the other phase. Neither of these assumption is valid for this transition.

VI.26 Determine the number of components for the following system: CH_3COONH_4 (s), CH_3COO^- (aq), NH_4^+ (aq), H_3O^+(aq), NH3 (aq),HO^- (aq), CH_3COOH (aq), H_2O (l), H_2O (g) taking hydrolysis into account.

R: C = 4

VI.27 What is the maximum number of phases in a system that contains NaCl and H_2O?

R: P = 4

VI.28 What is the variance for following systems:

a) a pure substance at critical point;

b) an azeotropic mixture.

R: a) F = 0; b) F = 1

VI.29 A person who has a superficial acquaintance with thermodynamics consults you about the following difficulties: I was under the impression that the free energy change for a system at equilibrium was supposed to be equal to zero. Yet the equilibrium free energy change for the reaction $N_2(g)+3\cdot H_2(g) \Leftrightarrow 2\cdot NH_3(g)$, is not equal to zero, but – 7.88 *kcal/mole* at 298 *K*. If the system is at equilibrium, why isn't the free energy change equal to zero?

R: The person does not understand the distinction between ΔG and ΔG^0. The criterion of equilibrium is that $\Delta G = 0$ and not $\Delta G^0 = 0$, only the equilibrium constant equal 1.

VI.30 At 1700 K and 1.10 atm, one g of chlorine occupies 1.96 liters. What are K_P, K_x and K_c for the reaction: $\frac{1}{2}\cdot Cl_2(g) = Cl(g)$? Assume ideal gas behavior.

R: $K_x = 0.185$; $K_P = 0.194$ atm$^{1/2}$; $K_c = 0.0164$ (mole l^{-1})$^{1/2}$

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VI.31 At 1600 K, the degree of dissociation of chlorine is 0.071 at 1 atm. What are are K_P, K_x and K_c for the reaction: $Cl_2(g) = 2 \cdot Cl(g)$? Assume ideal gas behavior.

R: $K_x = 0.0204$; $K_P = 0.0204$ atm; $K_c = 1.55 \times 10^{-4}$ mole l^{-1}

VI.32 The standard heats of formation of propil-benzene and propil-cyclohexane in gas phase are equal to 1870 respectively – 46220 cal·mole^{-1}, and Gibbs free energies are 32810 respectively 11330 cal·mole^{-1}. Determine log K_P at 287^{0}C for the reaction:

$n - C_6H_5C_3H_7(g) + 3 \cdot H_2(g) = n - C_6H_{11}C_3H_7(g)$

R: log $K_P = -0.745$

VI.33 The heat of formation for the reaction: $2 \cdot NOCl(g) \rightarrow 2 \cdot NO(g) + Cl_2(g)$, is almost independent of temperature and for the reaction at constant pressure $\Delta H = 18{,}000\, cal$. The standard entropies of the reactants at 25^{0}C are:

	NOCl	NO	Cl_2
$S^0_{298}\left(cal \cdot \deg^{-1} \cdot mole^{-1}\right)$	63.0	50.3	53.3

Estimate the value of the equilibrium constant K_P at 200^{0}C.

R: $K_{P_{473}} = 6.035 \times 10^{-3}\, atm$

VI.34 The e.m.f of the cell in which the following reaction takes place:

$Ag(s) + HgCl(s) = AgCl(s) + Hg(l)$ is 0.0455 V at 25^{0}C. The thermal coefficient of e.m.f is 3.38×10^{-4} V deg^{-1}. Calculate constant ΔG^0, ΔH^0 and ΔS^0.

R: $\Delta G^0 = -1050.4$ cal; $\Delta H^0 = 1274.9$ cal; $\Delta S^0 = -7.8$ cal·deg^{-1}

VI.35 Find the standard heat effect of the reaction:

$$\frac{1}{2} \cdot H_2 + \frac{1}{2} \cdot Hg_2Cl_2 = HCl(0.1m) + Hg$$

if for the cell: $Pt(H_2)/HCl(0.1m)/\frac{1}{2}Hg_2Cl_2/Hg$ we have $\varepsilon = 0.39946\ V$ and

$\left(\partial\varepsilon/\partial T\right) = 0.000115\ V \cdot \deg^{-1}$

R: $\Delta H^0 = -8420.34$ cal

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VI.36 An electrochemical cell is changing its volume with ΔV at passing of n electrochemical equivalents when is working at constant temperature and pressure. Show that: $\left(\frac{\partial \varepsilon}{\partial P}\right)_T = -\frac{\Delta V}{nF}$

VI.37 Show that the electromotive force of a galvanic cell does not depend on temperature when $T \to 0$.

R: When $T \to 0$, $\varepsilon = -\frac{\Delta H}{n \cdot F}$

VI.38 The distribution of picric acid between benzene and water at 18^0C is characterized by the following data ($mole \cdot l^{-1}$)

$c^{benz.}_{pic.acid}$	9.32×10^{-4}	2.25×10^{-3}	1.0×10^{-2}	2.0×10^{-2}	5.0×10^{-2}	1.0×10^{-1}	1.8×10^{-1}
$c^{water}_{pic.acid}$	4.17×10^{-4}	1.55×10^{-3}	1.42×10^{-2}	3.96×10^{-2}	1.56×10^{-1}	4.16×10^{-1}	9.63×10^{-1}

Find the equation of the distribution law.

R: $\frac{c^{water}_{pic.acid}}{\left(c^{benz.}_{pic.acid}\right)^{1.46}} = 12.6$ or $\frac{\left(c^{benz.}_{pic.acid}\right)^{1.46}}{c^{water}_{pic.acid}} = 0.0794$

VI.39 The solubility of methyl-amine is 8.49 times greater in water than in chloroform. Calculate the percentage of methyl-amine which remains in 1000 ml chloroform solution if it is submissive to successive extractions:

a) Four times with 200 ml water;

b) Two times with 400 ml water.

R: a) 1.88%; b) 5.17%

VI.40 Prove that the liquid-vapor equilibrium line in a one component system must always have a positive slope on a pressure temperature diagram.

R: $\frac{dP}{dT} = \frac{\Delta^v H}{T \cdot \Delta V} = \frac{\Delta^v H}{T \cdot \left(V^g - V^l\right)} = \frac{\Delta^v S}{V^g - V^l} = \frac{S^g - S^l}{V^g - V^l}$; $S^g > S^l$; $V^g > V^l$ $\Rightarrow \frac{dP}{dT} > 0$

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VI.41 The vapor pressure of ethene as a function of temperature is given by the equation:

$$\lg P(mmHg) = -\frac{834.13}{T} + 1.75 \cdot \lg T - 0.008357 \cdot T + 5.32340$$

Calculate the heat of vaporization of ethene, at its normal boiling point (169.46K).

R: $\Delta H = 3663.14\ cal \cdot mole^{-1}$

VI.42 The partial pressure of water vapor above an aqueous solution of ethanol, with molar fraction of alcohol $x_2^l = 0.042$ is P_1 = 16.8 mm Hg at 16.8°C. The vapor pressure of pure water at this temperature is P_1^0 = 17.5 mm Hg. Calculate the freezing point of the solution.

R: $t = -4.52^0 C$

VI.43 The solubility of methane in xilene at – 20°C and 50 mm Hg is 0.05 volumes of gas in normal conditions divided at solvent volume. Determine the solubility of methane (in same units) at – 20°C and 700 mm Hg and compare the obtained result with the experimental value: $x_{CH_4} = 0.68$.

R: $x_{CH_4} = 0.70$

VI.44 The temperature of crystallization for an eutectic mixture (naphthalene + benzene) is –3.6°C. Considering that on the entire concentration interval the solution has an ideal behavior, calculate the heat of fusion of naphthalene if the fusion temperature and heat of fusion of benzene are 278 K, respectively 2350 cal·mole^{-1}; for naphthalene the temperature of fusion are and 353 K. Compare the obtained result with the experimental value $\Delta^f H^0_{C_{10}H_8} = 4560\ cal \cdot mole^{-1}$

R: $\Delta^f H^0_{C_{10}H_8} = 4580\ cal \cdot mole^{-1}$

VI.45 Calculate the heat of dissolution of naphthalene in nitrobenzene knowing that at 25°C, the solubility of naphthalene is $x_2^l = 0.295$

R: $\Delta^f H^0_2 = 4629.80\ cal \cdot mole^{-1}$

VI.46 The heat of dissolution of phenol in benzene and pyridine are 2350 and – 630 cal·mole^{-1} respectively. Explain these results knowing that the melting heat of phenol is 2370 cal·mole^{-1}.

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R: From these data result that phenol dissociates in benzene and chemical interacts with pyridine.

VI.47 Calculate the ebullioscopic constant for water using the value 540 cal for the specific heat of vaporization.

R: $k_e = 0.51 \text{ deg} \cdot mole^{-1}$

VI.48 Calculate ebullioscopic constant of D_2O knowing that its boiling point is 101.42^0C and molar heat of vaporization is 9910 cal·mole^{-1}.

R: $k_e = 0.5626 \text{ deg} \cdot mole^{-1}$

VI.49 The latent heat of vaporization for benzene at its normal boiling point (80.2^0C) is 93 cal·g^{-1}. Calculate the elevation of the boiling point produced at the dissolution of 1 mole dissolved substance in 1000 g benzene.

R: $\theta_e = 2.66^0 C$

VI.50 Calculate the cryoscopic constant for water using the value 79.7 cal for the specific heat of fusion.

R: $k_c = 1.86 \text{ deg} \cdot mole^{-1}$

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REFERENCES

1. **CHEMICAL THERMODYNAMICS**, F. T. Wall, 1974, A course of study – the third edition, W. H. Freeman and Company, San Francisco
2. **INTRODUCTION TO CHEMICAL THERMODYNAMICS**, M. H. Everdell, 1965, Edition Revolucionaria, Instituto Cubano del Libro
3. **THE PRINCIPLES OF EQUILIBRIUM CHEMICAL** with applications in chemistry and chemical engineering, K. Denbigh, 1955, published by the Syndics of the Cambridge University Press, printed in Great Britain
4. **CHEMICAL THERMODYNAMICS**, M. Kh. Karapetyants, 1978, MIR Publishers
5. **THERMODYNAMIK**, Roland Reich, 1978, Verlag Chemie
6. **PHYSIKALISCHE CHEMIE**, E. A. Moelvyn-Hughes, 1970, Georg Thieme Verlag, Stuttgart
7. **FUNDAMENTALS OF CHEMICAL THERMODYNAMICS**, E. N. Yeremin, 1981, Mir Publishers
8. **MOLECULAR THERMODYNAMICS OF FLUID-PHASE EQUILIBRIA**, J. M. Prausnitz, R. Lichtenthaler, E. G. de Azevedo, 1999,Prentice Hall
9. **CHIMIE FIZICA**, D. Sandulescu, 1979, Ed. Stiintifica
10. **CHIMIE FIZICA**, Solomon Sternberg et all, 1981, Ed. Didactica si Pedagogica
11. **EXPERIMENTS IN PHISICAL CHEMISTRY**, J. M. Wilson, R. J. Newcombe, A. R. Denaro, R. M. W. Rickett, 1968, second revised and enlarged edition, Pergamon Press
12. **EXPERIMENTS IN PHISICAL CHEMISTRY**, D. P. Shoemaker, C. W. Garland, J. I. Steinfeld, J. W. Nibler, 1981, fourth edition, McGraw – Hill Book Company
13. **PRACTICAL PHYSICAL CHEMISTRY**, A. Findlay, J. A. Kitchener, 1954, Made and printed in Great Britain by William Clowes and Sons, limited, London and Beccles, Longmans, Green and CoLTD
14. **PROBLEMS IN PHYSICAL CHEMISTRY**, L. C. Labowitz, J. S. Arens, 1969, New York
15. **UNDERSTANDING PHYSICAL CHEMISTRY,** 1969, A. C. Adamson, New York
16. **PROBLEMS IN CHEMICAL THERMODYNAMICS**, R. J. Bearman, B. Chu, 1967, Addison-Wesley Publishing Company
17. **TERMODINAMICĂ CHIMICĂ**, R. Vîlcu, 1994, Editura Tehnică, Bucureşti

https://biblioteca-digitala.ro / https://unibuc.ro

18. **TERMODINAMICĂ CHIMICĂ – Îndrumar de lucrări practice**, R. Vîlcu, E. Tomuş, I. Găinar. I. Ciocăzanu, Z. Cenuşe, Şt. Perişanu, V. Meltzer, Gh. Anițescu, 1987, Centrul de multiplicare cursuri IPB
19. **CHIMIE FIZICĂ – Lucrări practice**, V. Isac, A. Onu, C. Tudoreanu, Gh. Nemțoi, 1995, Ştiința, Chişinău
20. **EXPERIMENTS IN CHEMICAL THERMODYNAMICS**, Daniela Bala, Ioan Găinar, 2002, Editura Universității din Bucureşti
21. **RECUEIL DE PROBLEMES DE TERMODYNAMIQUE CHIMIQUE**, M. Karapetiantz, 1976, Editions Mir, Moscou

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